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Persistent deNO_x Ability of CaAl₂O₄:(Eu, Nd)/TiO_{2-x}N_y Luminescent Photocatalyst

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Abstract

CaAl₂O₄:(Eu, Nd)/TiO_{2-x}N_y composite luminescent photocatalyst was successfully synthesized by a simple planetary ball milling process. Improvement of photocatalytic deNO_x ability of TiO_{2-x}N_y, together with the persistent photocatalytic activity for the decomposition of NO after turning off the light were realized, by coupling TiO_{2-x}N_y with long afterglow phosphor, CaAl₂O₄:(Eu, Nd). The novel persistent photocatalytic behavior was related to the overlap between the absorption wavelength of TiO_{2-x}N_y and the emission wavelength of the CaAl₂O₄:(Eu, Nd). It was found that CaAl₂O₄:(Eu, Nd)/TiO_{2-x}N_y composites provided the luminescence to persist photocatalytic reaction for more than 3 h after turning off the light.

Introduction

Hot photocatalytic research attention has been focused on titania (TiO₂), because of its chemical stability [1], excellent photocatalytic activity [2] and low cost. However, since titania has large band gap energy of about 3.2 eV corresponding to the wavelength of 387.5 nm, it is active under irradiation of only UV light less than 400 nm of wavelength. Since the content of UV light in sun light is less than 5% [3], the development of high performance visible light responsive photocatalyst which can use main part of sunlight or indoor light is highly desired [4-7]. Various modifications have been devoted to TiO₂ in extending the absorption edge into visible light and enhancing the photocatalytic activity [8-13], and one of them is doping TiO₂ with nitrogen because the band gap of titania could be narrowed by doping with nitrogen ion since the valence band of N2p band locates above O2p band [14].

The aluminate long afterglow phosphor (CaAl₂O₄:(Eu, Nd)) has characteristics of high luminescent brightness around 440 nm of wavelength, long afterglow time, good chemical stability and low toxicity [15,16]. Therefore, the coupling of TiO₂ with CaAl₂O₄:(Eu, Nd) was expected to prolong the photocatalytic activity even after turning off the light by using the persistent emitting luminescence of the long afterglow phosphor as a light source of TiO₂ photocatalyst. However, TiO₂

possessing a large bandgap energy ca. 3.2 eV can not be effectively excited by the visible light luminescence of 440 nm from CaAl₂O₄:(Eu, Nd). Recently, the combinations of TiO₂ photocatalyst with other long afterglow materials such as BaAl₂O₄:(Eu, Dy) [17] and Sr₄Al₁₄O₂₅:(Nd, Eu) [18] were also reported. However, the emission wavelengths of these phosphors around 495 nm [19] and 488 nm, respectively, are also too long to excite TiO₂ photocatalyst. Actually, it was reported that BaAl₂O₄:(Eu, Dy)/TiO₂ and Sr₄Al₁₄O₂₅:(Nd, Eu)/TiO₂ coupled compounds showed photocatalytic performance for the oxidation of gaseous benzene and RhB solution, respectively, under UV light irradiation, but no noticeable degradation was observed after turning off the light [17].

In the present research, we firstly provided a direct evidence for such persistent photocatalytic deNO_x system, by the coupling of long afterglow phosphor CaAl₂O₄:(Eu, Nd) with brookite type nitrogen-doped titania (TiO_{2-x}N_y), which was produced by a hydrothermal reaction [20,21]. Brookite phase nitrogen-doped titania possessed band gap of ca. 2.34 eV and showed excellent photocatalytic deNO_x ability even under visible light irradiation of wavelength >510 nm [20]. In comparison with anatase and rutile phase nitrogen-doped titania, brookite phase nitrogen-doped titania photocatalyst has seldom been reported, however, it is expected to be a potential novel photocatalyst.

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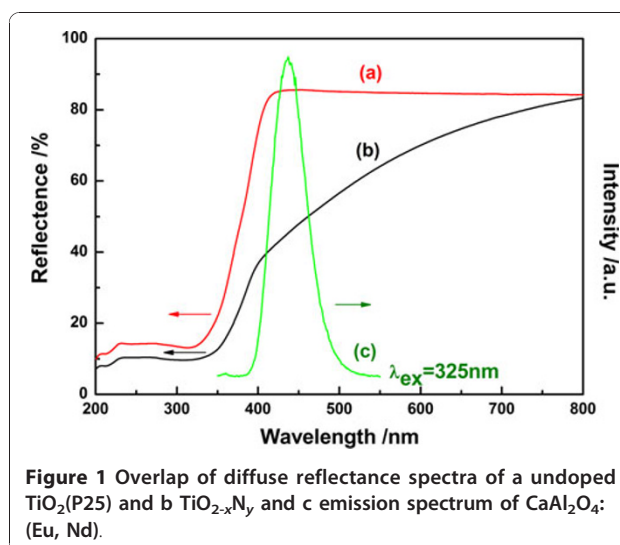
Experimental Section

$\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ powders with the particle size of $13.9 \mu\text{m}$ (D_{50}) were purchased from Nemoto Co. Ltd. Other chemicals were purchased from Kanto Chem. Co. Inc. Japan and were used as received without further purification. $\text{TiO}_{2-x}\text{N}_y$ nanoparticles with brookite phase were synthesized by hydrothermal reaction using TiCl_3 as titanium source and HMT (hexamethylenetetramine) as nitrogen source at pH 7 and 190°C for 2 h [20]. Brookite phase $\text{TiO}_{2-x}\text{N}_y$ nanoparticles were mixed with desired amounts of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ powders followed by planetary ball milling at 200 rpm for 20 min. The mass ratio of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$: $\text{TiO}_{2-x}\text{N}_y$ or P25 TiO_2 was kept at 3/2. For comparison, undoped titania (Degussa P25) was also coupled with $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ by the completely same manner. The UV-vis diffuse reflectance spectra were obtained using a UV-vis spectrophotometer (Shimadzu, UV-2450). The time dependence of photoluminescence spectra and intensity were measured by a spectrofluorophotometer (Shimadzu RF-5300P).

The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm^3 of internal volume) during the photo-irradiation of a constantly flowing 1 ppm NO/50 vol% air mixed (balance N_2) gas ($200 \text{ cm}^3 \text{ min}^{-1}$). 0.16 g of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$, $\text{TiO}_{2-x}\text{N}_y$ or $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{P25}$ photocatalyst material was placed in the same area of a hollow of $40 \times 30 \times 0.5 \text{ mm}$ on a glass holder plate and set in the bottom center of the reactor. A 450 W high-pressure mercury lamp was used as the light source, where the inner cell had water flowing through a Pyrex jacket between the mercury lamp and the reactor. The light of $\lambda < 290 \text{ nm}$ wavelength was cut off by Pyrex glass [20-22]. Before light irradiation, the NO gas was continuously flowed through the reactor for 10 min to achieve adsorption balance. Then, the light was irradiated for 30 min to realize the steady status of the photocatalytic NO degradation and let long afterglow phosphor $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ absorb enough exciting energy. After that, the light was switched off, while the NO gas was flowed further for 3 h.

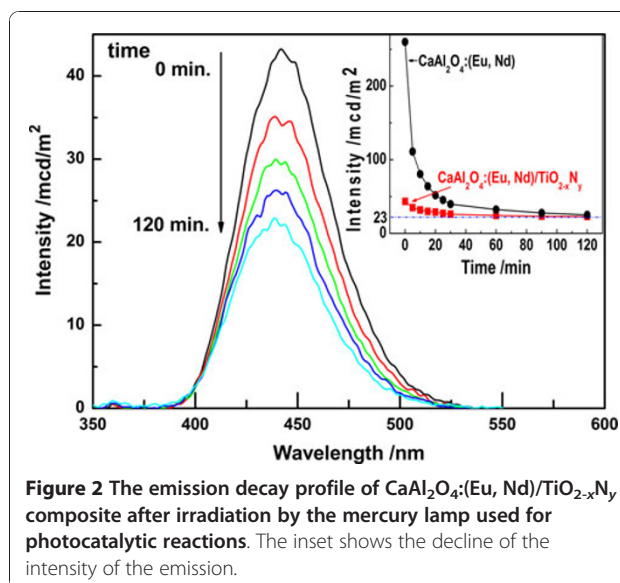
Results and Discussion

Figure 1 shows the diffuse reflectance spectra of undoped and nitrogen-doped titania and the emission spectrum of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$. $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ emitted blue luminescent light with a peak of 440 nm in wavelength by UV light irradiation (325 nm). Although undoped titania absorbed only UV light of the wavelength less than 400 nm, nitrogen-doped titania showed absorption of visible light up to 700 nm showing a nice overlap between the diffuse reflectance spectrum of



$\text{TiO}_{2-x}\text{N}_y$ and the emission spectrum of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$. Therefore, it implied the potential possibility of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ composite as the luminescent assisted photocatalyst which use the long after glow from the phosphor as the light source of the photocatalyst. Our previous research proved that nitrogen doped titania could be induced the photocatalytic activity by such weak LED light as 2.0 mW/cm^2 with long wavelength of 627 nm [23,24]. This result also strongly implied the potential application of the composite as luminescent assisted photocatalyst material.

Figure 2 shows the emission decay profile of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ composite. The composite showed an emission spectrum peaked at 440 nm, which was almost identical to that of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$, attributed to the typical $4f^6 5d^1 - 4f^7$ transition of Eu^{2+} [16]. This indicated



that the even if 40% brookite $\text{TiO}_{2-x}\text{N}_y$ was coated on the surface of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ particles, comparatively strong luminescence property of the composite was kept. Although the emission intensity decayed with time, the emission intensity about 23 mcd/mm^2 was retained even after 2 h.

Figure 3 shows the photocatalytic NO destruction behaviors of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$, $\text{TiO}_{2-x}\text{N}_y$ and $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{undoped TiO}_2$ (P25) under UV light irradiation and after turning off the light. It was obvious that all the samples possessed excellent photocatalytic deNO_x activity under UV light irradiation. Although the effect was very limited, it could be actually confirmed from the data of Figure 3a, b that under irradiation of high pressure mercury lamp (The data between *light on* and *light off*), $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ luminescent photocatalyst exhibit better photocatalytic activity than that of $\text{TiO}_{2-x}\text{N}_y$.

The characterization system used in the present research was similar to that of the Japanese Industrial Standard which was established at the beginning of 2004 [25]. In this JIS standard, it is recommended that the photocatalytic activity of photocatalyst should be characterized by measuring the decrease in the concentration of NO at the outlet of a continuous reactor. One ppm of NO gas with a flow rate of $3.0 \text{ dm}^3/\text{min}$ is introduced to a reactor then irradiated by a lamp with light wavelength of 300–400 nm. The mechanism of photocatalytic deNO_x had been researched carefully by M.Anpo [26]. During the deNO_x photocatalytic reaction, the nitrogen monoxide reacts with these reactive oxygen radicals, molecular oxygen, and very small amount of water in air to produce HNO_2 or HNO_3 . It was confirmed that about 20% of nitrogen monoxide was decomposed to nitrogen and oxygen directly [26] Because a continuous reaction system was utilized in the

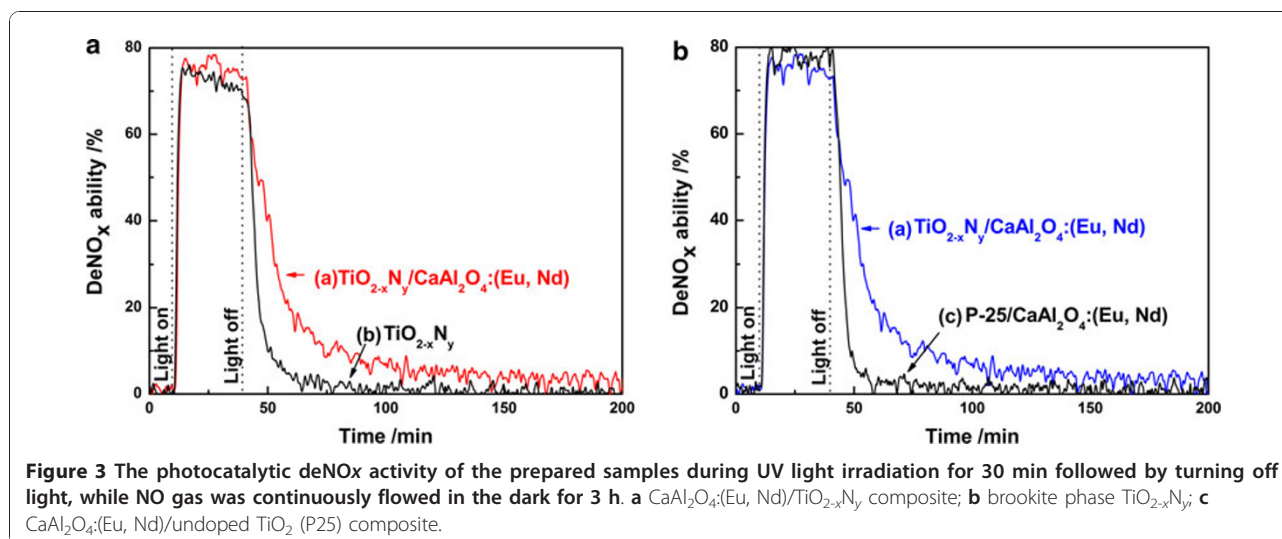
deNO_x characterization [20,21], after turning off the light, it took about 10 min (total 50 min from the start of the characterization) to achieve diffusion balance and return to the initial NO concentration.

The degree of NO destruction by $\text{TiO}_{2-x}\text{N}_y$ and $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{undoped TiO}_2$ (P25) immediately decreased after turning off the light, however, as-expected, $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ retained the NO destruction ability for about 3 h. Since the decay profile of the NO destruction degree of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ was similar to the emission decay profile shown in Figure 2, it might be concluded that the emission by $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ was used as a light source to excite $\text{TiO}_{2-x}\text{N}_y$ photocatalyst. It was also confirmed that $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ composite consisted of 40% brookite $\text{TiO}_{2-x}\text{N}_y$ (mass ratio of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y = 3/2$) possessed the best performance after turning off the light.

Present results indicate that the combination of $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ and $\text{TiO}_{2-x}\text{N}_y$ is a key point to realize the persistent catalytic activity even after turning off the light. In addition, it is well known that the combination of the two different band structure compounds may cause the charge transfer on the photocatalyst surface to depress the recombination of photo-induced electrons and holes, which is helpful for the improvement of photocatalytic activity [27,28]. This novel system provides a possibility of atmosphere purification not only in day time, but also in night time. A promising strategy involves coupling of visible light induced photocatalyst with long afterglow phosphor might be established. It is a new concept for the photocatalyst synthesis and applications.

Conclusion

A novel $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ composite luminescent photocatalyst was successfully synthesized. Not



only the UV-light induced photocatalytic activity, but also the persistent catalytic ability after turning off the light was realized successfully. The $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})/\text{TiO}_{2-x}\text{N}_y$ composite photocatalyst provided enough luminescence intensity for the photocatalytic reaction for more than 3 h after turning off the light source.

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References

1. Li Y, Sun X, Li H, Wang S, Wei Y: *Powder Technol* 2009, **194**:149-152.
2. Kim D, Kwak S: *Appl Catal A-Gen* 2007, **323**:110-118.
3. Tafen D, Wang J, Wu N, Lewis J: *Appl Phys Lett* 2009, **94**:093101.
4. Yin S, Zhang Q, Saito F, Sato T: *Chem Lett* 2003, **32**:358-359.
5. Yin S, Yamaki H, Komatsu M, Zhang Q, Wang J, Tang Q, Saito F, Sato T: *J Mater Chem* 2003, **13**:2996-3001.
6. Wang J, Yin S, Zhang Q, Saito F, Sato T: *J Mater Chem* 2003, **13**:2348-2352.
7. Aita Y, Komatsu M, Yin S, Sato T: *J Solid State Chem* 2004, **177**:3235-3238.
8. Moon J, Yun C, Chung K, Kang M, Yi J: *Catal Today* 2003, **87**:77-86.
9. Cho Y, Kyung H, Choi W: *Appl Catal B: Environ* 2004, **52**:23-32.
10. Kaur S, Singh V: *Ultrason Sonochem* 2007, **14**:531-537.
11. Liu S, Chen X: *J Hazard Mater* 2008, **152**:48-55.
12. Chen F, Zou W, Qu W, Zhang J: *Catal Commun* 2009, **10**:1510-1513.
13. Jirapat A, Puangrat K, Supapan S: *J Hazard Mater* 2009, **168**:253-261.
14. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y: *Science* 2001, **293**:269-271.
15. Chang C, Xu J, Jiang L, Mao D, Ying W: *Mater Chem Phys* 2006, **98**:509-513.
16. Zhao C, Chen D: *Mater Lett* 2007, **61**:3673-3675.
17. Li S, Wang W, Chen Y, Zhang L, Guo J, Gong M: *Catal Commun* 2009, **10**:1048-1051.
18. Zhang J, Pan F, Hao W, Ge Q, Wang T: *Appl Phys Lett* 2004, **85**:5778-5780.
19. Chen X, Ma C, Li X, Shi C, Li X, Lu D: *J Phys Chem C* 2009, **113**:2685-2689.
20. Yin S, Aita Y, Komatsu M, Wang J, Tang Q, Sato T: *J Mater Chem* 2005, **15**:674-682.
21. Yin S, Hasegawa H, Maeda D, Ishitsuka M, Sato T: *J Photochem Photobiol A: Chem* 2004, **163**:1-8.
22. Gateshki M, Yin S, Ren Y, Petkov V: *Chem Mater* 2007, **19**:2512-2518.
23. Yin S, Zhang P, Liu B, Liu X, Sato T, Xue D, Lee S: *Res Chem Intermed* 2010, **36**:69-75.
24. Yin S, Liu B, Zhang P, Morikawa T, Yamanaka K, Sato T: *J Phys Chem C* 2008, **112**:12425-12431.
25. Japanese Industrial Standard (JIS R 1701-1:2004(J)), Test method for air purification performance of photocatalytic materials—part 1: removal of nitric oxide, Japanese Standards Association, Established on 20-Jan-2004.
26. Anpo M: "Recent Development on Visible Light Response Type Photocatalyst". NTS, Tokyo; 2002, 9, (ISBN4-86043-009-03).
27. Wang J, Xie Y, Zhang Z, Li J, Chen X, Zhang L, Xu R, Zhang X: *Sol Energy Mat Sol C* 2009, **93**:355-361.
28. Kamei M, Miyagi T, Ishigaki T: *Chem Phys Lett* 2005, **407**:209-212.

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