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Persistent luminescence assisted photocatalytic properties of $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ and $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$

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ABSTRACT

The systematic experiments of photocatalytic degradation of NO gas and acetaldehyde were carried out by using novel composites consisting of $TiO_{2-x}N_y$ loaded on two types of long afterglow phosphor, $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy). The two kinds of composites were prepared in a sequence of the same procedures, which involved reactions of $TiCl_3$ and hexamethylenetetramine (HMT) mixed solution at 190 °C for 2 h to precipitate nano-size $TiO_{2-x}N_y$ particles, followed by mixing the $TiO_{2-x}N_y$ with a micro-size $CaAl_2O_4$:(Eu,Nd) or $Sr_4Al_{14}O_{25}$:(Eu,Dy) particles by a facile planetary ball milling to yield $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ or $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$ composites. Both composites showed the persistent photocatalytic degradation of NO and acetoaldehyde after turning off the light. $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ showed higher persistent NO destruction ability in dark after turning off the light, while $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$ is excellent in CH_3CHO removal. The difference in the photocatalytic activity observed for $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ and $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$ might be attributed to the difference in the emission property.

1. Introduction

Visible light induced photocatalysis has attracted intensive interest due to its potential applications in environmental pollutants purification and solar energy conversion by utilizing visible light in solar and/or indoor light [1–6]. The leading candidate photocatalyst, pure TiO_2, however, has a bandgap of 3.0–3.2 eV, which is too wide to absorb the most portion of solar energy and limits its solar applications. Nonmetal doping, especially N doping, has displayed promising results in extending the light absorption of TiO_2 into the visible-light region, 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 [7].

Another way to enhance the photocatalytic activity of TiO_2N_y is the formation of charge transfer complex of TiO_2 and another material, which can absorb solar light [8–12]. 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 [13,14]. The long afterglow phosphor such as $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy) are potential candidate materials to combine with TiO_2N_y. In the long afterglow phosphor/TiO_2N_y composite, the light energy is accumulated in long afterglow phosphor, and the accumulated light energy let long afterglow phosphor emit eye-visible luminescence in dark, which will be used as a light source for persistent photocatalysis. Several long afterglow phosphor/TiO_2 composites were fabricated, but the persistent photocatalytic activities of them were modest [15,16]. In a previous paper [17], it was reported that $TiO_{2-x}N_y$ coupled with $CaAl_2O_4$:(Eu,Nd) possessed persistent $deNO_x$ ability for more than 3 h after turning off light. It seemed that the luminescence responsive efficiency plays a key role in the persistent photocatalytic activity [18]. It was also found that the composite of long afterglow phosphor/$TiO_{2-x}N_y$ with brookite phase showed excellent performance for the degradation of NO [34], however, the physicochemical and optical properties of them are not clarified in detail.

In order to further investigate the luminescence responsive efficiency of composite photocatalyst, $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy), being two the most popular commercial long afterglow phosphors with luminescence around 440 nm and 490 nm of wavelength respectively, were used to couple with brookite type $TiO_{2-x}N_y$, which showed excellent visible-light responsiveness [23–25,40]. The two types of aluminate long afterglow phosphors have characteristics of good chemical stability and low toxicity [19,20], and can emit high intensity of the eye-visible luminescence for more than 10 h [21,22].

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2. Experimental

2.1. Preparation of photocatalysts

$CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy) powders with particle size (D_{50}) of 13.9 and 16.4 μm, respectively, were purchased from Nemoto Co. Ltd. Other chemicals were purchased from Kanto Chem. Co. Inc. Japan and were used as received without further purification. $TiO_{2-x}N_y$ nanoparticles were synthesized by using $TiCl_3$ as titanium source and hexamethylenetetramine (HMT) as a nitrogen source. After putting these reagents and methanol into a Teflon® tube inserted stainless sealed reactor, the solution was heated at 190 °C and pH 7 for 2 h [23,26,27]. The precipitates were collected by centrifugation, carefully washed with water, and finally vacuum dried at 60 °C overnight. $TiO_{2-x}N_y$ nanoparticles were then mixed with $CaAl_2O_4$:(Eu,Nd) or $Sr_4Al_{14}O_{25}$:(Eu,Dy) micro-particles by planetary ball milling treatment with 200 rpm for 20 min, with the mass ratio of $TiO_{2-x}N_y$ to $CaAl_2O_4$:(Eu,Nd) or $Sr_4Al_{14}O_{25}$:(Eu,Dy) as 2:8, 3:7, 4:6, and 5:5. The product was assigned as $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ and $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$. For comparison, commercial undoped titania sample (Degussa P25) was also utilized and characterized.

2.2. Analysis

The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized CuKα radiation. The UV–vis diffuse reflectance spectra (DRS) were obtained using a UV–vis spectrophotometer (Shimadazu, UV-2450). The time dependence of photoluminescence (PL) spectra and intensity were measured by a spectrofluorophotometer (Shimadzu RF-5300P). The nitrogen adsorption–desorption isotherm was conducted on a surface area and pore size analyzer (Quantachrome Instruments, NOVA 4200e), and the specific surface area was determined by BET method. The water-resistance abilities of long afterglow phosphors were evaluated as follows: 0.30 g of samples were dispersed in 5 mL of deionized water, then vacuum dried at 60° overnight.

2.3. Photocatalytic activity evaluation

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 cm^3 min^{-1}). 0.16 g of sample was placed in the same area of a hollow of 40 mm × 30 mm × 0.5 mm on a glass holder plate and set in the bottom center of the reactor. An artificial solar light (HAL-302, Asahi Spectra Co. Ltd., Japan) with 69.3 W/m^2 was used as the light source. Before light irradiation, the NO gas was continuously flowed through the reactor for 10 min to achieve diffusion and adsorption balance. Then, the light was irradiated for 30 min to realize the steady state of the photocatalytic NO degradation and let long afterglow phosphor absorb enough exciting energy. After that, the light was switched off, while the NO gas was flowed further for 3 h.

The photocatalytic activity was also evaluated by measuring the changes in the concentrations of acetaldehyde and the decomposition product, CO_2, for acetaldehyde degradations. In order to obtain a homogeneous sample film for photocatalytic characterization, 0.3 g of sample powder was sufficiently mixed with 0.48 g xylene and 0.48 g 2-butanol, then dispersed on a glass substrate with an area of $\pi \times 25$ mm^2. The sample was then heated at 140 °C for 30 min to evaporate the organic solvents. After irradiation with a 10 W black light for 1 h to eliminate the adsorbed organics on the surface, the sample was kept under black light irradiation with the wavelength of 325 nm for 30 min, then, was placed in the reaction vessel without irradiation. The experiment was started after injecting 10 μL of acetaldehyde and proceed in the dark without lamp irradiation. Then, about 5.0 mL of gas was withdrawn from the reaction vessel through the injection hole every 30 min to determine the concentrations of the remaining acetaldehyde and generated CO_2 using a gas chromatograph (GC-2014 SHIMADZU).

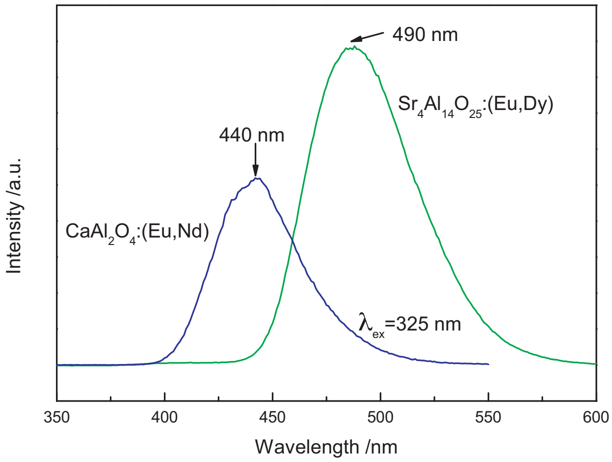

Fig. 1. Emission spectra of $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy) (λ_{ex} = 325 nm).

3. Results and discussion

3.1. BET specific surface area

As a result of the loading of the fine particles of $TiO_{2-x}N_y$, the prepared $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ and $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$ composite samples showed quite high specific surface areas of 243–273 and 36.4–95.5 m^2/g, respectively, as shown in Table S1. The specific surface area of $CaAl_2O_4$:(Eu,Nd)/$TiO_{2-x}N_y$ composite did not change so much when changing the amount of $TiO_{2-x}N_y$, while the specific surface area of $Sr_4Al_{14}O_{25}$:(Eu,Dy)/$TiO_{2-x}N_y$ increased with increasing the amount of $TiO_{2-x}N_y$.

3.2. XRD characterization

The X-ray diffraction pattern of the as-prepared $TiO_{2-x}N_y$ is shown in Fig. S1. All the peaks can be indexed based on the brookite type TiO_2 (JCPDS Card 29-1360).

3.3. Optical property

The emission spectra of $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy) were detected by UV light (λ_{ex} = 325 nm) irradiation as shown in Fig. 1. $CaAl_2O_4$:(Eu,Nd) [30,31] emitted blue luminescent light with a peak of 440 nm in wavelength, which possess higher energy than that of green luminescent light with a peak of 490 nm in wavelength emitted from $Sr_4Al_{14}O_{25}$:(Eu,Dy) [32,33], where the intensity of the luminescence from $Sr_4Al_{14}O_{25}$:(Eu,Dy) was much higher. The $CaAl_2O_4$:(Eu,Nd) and $Sr_4Al_{14}O_{25}$:(Eu,Dy) show the emission spectra peaked at 440 nm and 490 nm, respectively, which are attributed to the typical $4f^65d^1$-$4f^7$ transition of Eu^{2+} [20]. On the other hand, according to the DRS spectra shown in Fig. S2, although undoped titania (P25) absorbed only UV light of the wavelength less than 400 nm, $TiO_{2-x}N_y$ showed absorption of visible light up to 700 nm. Therefore, it implied the potential ability of $TiO_{2-x}N_y$ to use the persistent luminescence emitting from the phosphors as the light source. Our previous research proved that