



Enhanced photocatalytic NO_x decomposition of visible-light responsive F-TiO₂/(N,C)-TiO₂ by charge transfer between F-TiO₂ and (N,C)-TiO₂ through their doping levels

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ABSTRACT

Composite type photocatalyst F-TiO₂/(N,C)-TiO₂ consisted of anatase-type TiO₂ with fluorine-doping (F-TiO₂) and TiO₂ with nitrogen and carbon-doping ((N,C)-TiO₂) was prepared by simple physical mixing to exhibit higher visible-light responsive photocatalytic nitrogen oxide (NO_x) decomposition activity than those of F-TiO₂ and (N,C)-TiO₂. Transient absorption measurement clarified that the composite possessed longer carrier lifetime compared to that of each material (F-TiO₂ or (N,C)-TiO₂), resulting in higher photocatalytic activity. In the composite, photoexcited holes and electrons, which are not in impurity level but in valence and conduction band, respectively, should photocatalytically decompose NO_x, judging from the redox potential of O₂/O₂⁻ and the band positions of F-TiO₂ and (N,C)-TiO₂. The mechanism for higher visible-light photocatalytic activity, or longer carrier lifetime can be explained by charge transfer between F-TiO₂ and (N,C)-TiO₂ through their impurity levels. The charge transfer should make photoexcited carries spatially separated to enhance the photocatalytic activity.

1. Introduction

Utilization of photocatalysts is one of the way for solution of recent energy and environment problems, because they can induce redox reactions under solar light which almost permanently reaches to the earth [1]. The redox reactions by photocatalysts can lead to many applications including self-cleaning, decomposition of substance and water-splitting [2,3]. Titanium dioxide (TiO₂) is one of the metal oxide semiconductors with high photocatalytic activity [4,5]. Because TiO₂ is chemical and physical stable, low-cost and easy to be synthesized, it was widely studied and practically applied. Among various crystal structure of TiO₂, anatase type TiO₂ has been known as an excellent photocatalyst. However, band gap of anatase-type TiO₂ is too wide (~3.2 eV), and anatase-type TiO₂ possesses no visible-light photoresponsivity [6]. Therefore, many efforts have been paid for creation of visible-light responsivity in TiO₂.

Some elements have been doped to TiO₂ to realize visible-light photoresponsivity [7–11]. Recently, much attention has been given to anion doping including nitrogen-, fluorine-, and carbon-doping to TiO₂ to form mixed-anion materials, because it can easily prepare visible-light responsive photocatalysts [12]. Nitrogen doping into TiO₂ makes

impurity level at shallower potential than the valence band (VB) maximum of TiO₂ [13–18]. In the case of fluorine doping, Ti³⁺ is formed by reduction of Ti⁴⁺ as a counterpart of F⁻ and the Ti³⁺ impurity level locates at deeper potential than the conduction band (CB) minimum of TiO₂ [18–20]. Carbon can be doped to both anionic and cationic sites of TiO₂ to form various types of impurity level between its band gap [15,18,21,22]. Such doping decrease excitation energy to induce visible-light responsivity. Because each dopant can lead to formation of different impurity level, we can design visible-light responsive TiO₂ with various band structures by selection or combination of various dopants. However, impurity level can sometimes work as a recombination centre, and its prevention is surely needed.

Formation of composite can suppress electron-hole recombination, because charge transfer can occur between two types of semiconductors with different band structures [23–25]. The excited electrons and holes transfer at the interface of composite can be categorized into two types; double-charge transfer mechanism and Z scheme mechanism. In the case of double-charge transfer mechanism (Scheme 1a), photoexcited electrons in CB of semiconductor B transfer to CB of semiconductor A, and photoexcited holes in VB of semiconductor A transfer to VB of semiconductor B. Because electrons and holes accumulate in CB of

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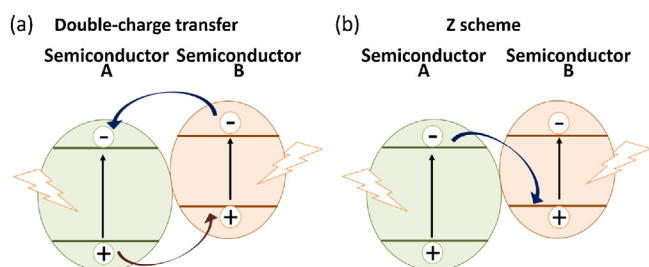
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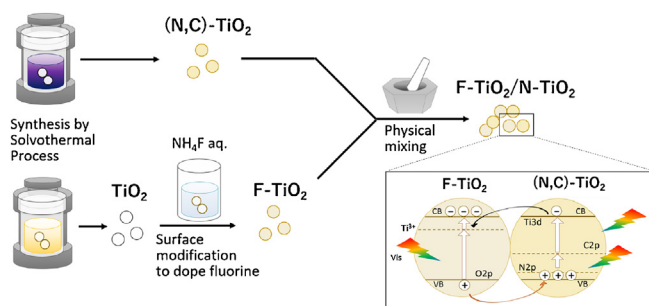


Scheme 1. Schematic diagram of electron–hole separation at the interface of composite; (a) double-charge transfer mechanism and (b) Z scheme mechanism.

semiconductor A and VB of semiconductor B, respectively, recombination between excited electrons and holes can be suppressed.

In the case of Z scheme mechanism (Scheme 1b), photoexcited electrons in CB of semiconductor A transfer to VB of semiconductor B, and combine with photoexcited holes in VB of semiconductor B. Consequently, electrons and holes are separated and accumulate in CB of semiconductor B and VB of semiconductor A, respectively. Recently, some semiconductors with doping have been applied as a component of such composites, and the composites have possessed distinguished photocatalytic activity [26–29]. However, effect of their impurity level induced by doping on catalytic activity of composites has not been understood exactly. Such understanding can enable to precisely design photocatalytic composite materials and these photoreaction processes.

In this study, we demonstrate the effect of impurity level of semiconductor on photocatalytic activity of composite. Anatase-type TiO_2 photocatalysts with anion doping were used as a component of photocatalyst composites. Because anatase-type TiO_2 with different dopants possess different impurity level with the same conduction and valence bands, we can easily focus only the effect of the impurity level. Three types of anatase-type TiO_2 doped with various anions, such as fluorine-doped TiO_2 (F- TiO_2), carbon-doped TiO_2 (C- TiO_2) and nitrogen and carbon-doped TiO_2 ((N,C)- TiO_2), were used as the component of photocatalyst composites; In addition, anatase-type TiO_2 without doping was also synthesized for comparison. By simply mixing any two of those materials, such as TiO_2 and (N,C)- TiO_2 (TiO_2 /(N,C)- TiO_2), F- TiO_2 and (N,C)- TiO_2 (F- TiO_2 /(N,C)- TiO_2), F- TiO_2 and C- TiO_2 (F- TiO_2 /C- TiO_2), C- TiO_2 and (N,C)- TiO_2 (C- TiO_2 /(N,C)- TiO_2), various kind of composites were prepared, and their photocatalytic NO_x decomposition activities were evaluated under visible- and UV light irradiation (Scheme 2). Because the photocatalytic activity of F- TiO_2 /(N,C)- TiO_2 was higher than that of F- TiO_2 and (N,C)- TiO_2 , the carrier dynamics of the composite was analysed for understanding the role of their impurity levels. In addition, the effect of mixing ratio of F- TiO_2 /(N,C)- TiO_2 on the photocatalytic activity was also investigated. From those results, we discussed about the photo-reaction process and the mechanism for the effect of impurity level on photocatalytic activity of the composite.



Scheme 2. Schematic synthesis flow of F- TiO_2 /(N,C)- TiO_2 .

2. Experimental

2.1. Synthesis of TiO_2 with and without doping and preparation of their composites

TiO_2 was synthesized by a solvothermal process. First, titanium tetraisopropoxide (Kanto Chemical Co., Inc., 1.2 mL) was added to a mixed solvent including ethanol (Kanto Chemical Co., Inc., 8 mL) and acetic acid (Kanto Chemical Co., Inc., 2 mL), and then stirred for 30 min. After that, the mixture was transferred to a Teflon container with internal volume of 100 mL, and the container was put in stainless steel autoclave. The autoclave was heated at 240 °C for 24 h with rotation at 100 rpm. After the treatment, the mixture was filtrated, and white powders were obtained. The white powders were washed with distilled water and ethanol, and dried at 60 °C overnight. The obtained sample was denoted as TiO_2 . F- TiO_2 was prepared by treatment of the obtained TiO_2 with ammonium fluoride (NH_4F) aqueous solution [30]. The obtained TiO_2 (7.2 g) was added to 0.11 M NH_4F aqueous solution (Kanto Chemical Co., Inc., 8 mL) and the dispersion was stirred for 24 h at room temperature. After the stirring, the dispersion was filtrated to obtain a white precursor. After washing and drying, the white powders were put into alumina crucible and calcined at 300 °C for 2 h in air to obtain a beige colour of sample, which was denoted as F- TiO_2 . (N,C)- TiO_2 was synthesized on the basis of our previous report [31]. A solution of 20 wt % Titanium (III) chloride (Kanto Chemical Co., Inc., 21.5 mL) and hexamethylenetetramine (Kanto Chemical Co., Inc., 10 g) were mixed with methanol (Wako Co., 25 mL). The mixture was transferred to a Teflon container in stainless steel autoclave, and heated at 190 °C for 2 h. After filtration, the sample was washed and dried overnight. The obtained beige powder was denoted as (N,C)- TiO_2 . C- TiO_2 was also synthesized on the basis of our other previous report [32]. Firstly, titanium(IV) tetrabutoxide (Kanto Chemical Co., Inc., 2.5 mL) was mixed with ethanol (8 mL) and then the mixture was stirred for 30 min. Then, a mixed solvent including from ethanol (10 mL) and distilled water (15 mL) was added to the mixture, and stirred for 30 min. To carry out the solvothermal reaction, the mixture was introduced into a Teflon-sealed autoclave. After heating at 190 °C for 2 h, white powders as precursor for C- TiO_2 were obtained after filtration. The white powders were heated at 265 °C for 2 h in air to produce C- TiO_2 . For the preparation of various composites, any two kinds of TiO_2 -based single materials were physically mixed by using agate mortar. Four kinds of composites including F- TiO_2 /(N,C)- TiO_2 , F- TiO_2 / TiO_2 , (N,C)- TiO_2 /C- TiO_2 and F- TiO_2 /C- TiO_2 were obtained. Basically, the mixing ratio of the two materials in the composites was 1:1.

2.2. Characterization

The crystalline phases and crystallite size of samples were identified by powder X-ray diffraction analysis (XRD, Bruker AS, Inc., D2PHASER) using $\text{Cu K}\alpha$ radiation. The size and shape of the obtained samples were observed by transmission electron microscopy (TEM, JEOL Inc., JEM-2000EXII). The specific surface areas were calculated from N_2 absorption measurements by the BET equation (Quantachrome Instruments Japan LLC, NOVA 4200e). The UV–vis diffuse reflectance spectra (DRS) were measured by using a UV–vis spectrophotometer (JASCO Co., V-670). The composition and chemical bonding state of samples were detected by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Inc., PHI5600).

2.3. Measurement of transient absorption spectra

Microsecond time-resolved visible to mid-IR absorption measurements were performed by using the custom-built spectrometers, as reported in our previous paper [33]. Briefly, in the mid-IR region (6000–1000 cm^{-1}), the probe light emitted from an IR source was focused on the sample, and the transmitted light was monochromated

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