

C₃N₄-Based Photocatalysts for HCHO Decomposition with Water Vapor under Visible Light Irradiation

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C₃N₄ を基材とした可視光応答型光触媒による 水蒸気含有下での気相 HCHO 光分解

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Abstract

From a cyanamide (NH₂CN) powder as a precursor, C₃N₄-based photocatalysts can easily be prepared by calcination at 573-673 K in argon or air flowing atmosphere. In a fixed bed flow reaction under photoirradiation by mercury lamp or LED light, the C₃N₄-Based photocatalysts have been applied for HCHO decomposition in air flowing with water vapor. By calcination of cyanamide at 623 K under NH₃-N₂ atmosphere, g-C₃N₄ was obtained with high crystallinity. However, the crystallinity became mow by washing with H₂O or HCl solution. It is suggested that conventional preparation g-C₃N₄ is available by calcination of cyanamide in Ar flow at 623 K because of durable crystallinity for H₂O. Over the C₃N₄ calcined in Ar, high photocatalytic activity for HCHO decomposition with water vapor, which is possibly based on the VIS absorption (at around 2.47 eV), was exhibited. Durable photoactivity for HCHO decomposition could be shown by preparation of C₃N₄ supported on TiO₂.

Key Words: Carbon nitride (C₃N₄), Cyanamide (NH₂CN), Visible Light Photocatalyst, VOC Photodecomposition, Visible Light LED Irradiation

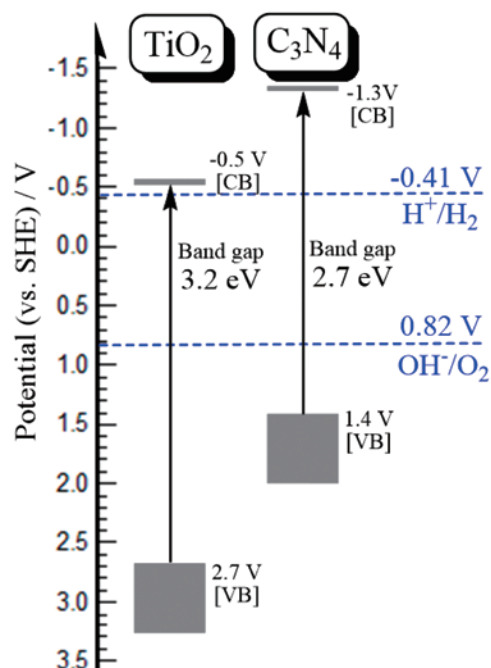
1. Introduction

As well known, anatase-type titanium dioxide

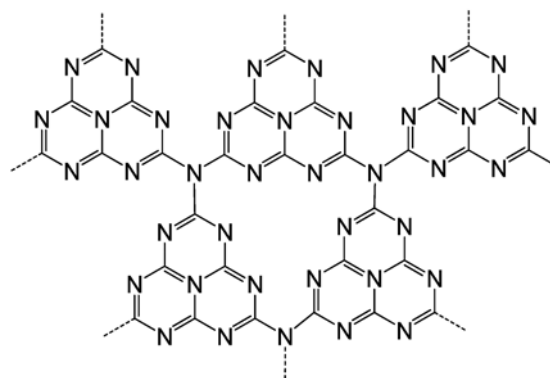
(TiO₂) shows a typical high photocatalytic activity in presence of O₂ and/or H₂O¹⁻²⁾. Since the

“Honda-Fujishima Effect” on the electrochemical photolysis of water with n-type TiO_2 electrode was discovered³⁾, the photocatalytic activity of TiO_2 have also attracted. Then the TiO_2 photocatalyst has been studied by many researchers on its photocatalytic mechanism, conditions for high activation, and applications about its practical use. On the other hand, ultraviolet irradiation is mandatory as a fundamental subject of TiO_2 photocatalysts due to the band-gap (3.0–3.2 eV). Then, many studies about S- or N-doped anatase TiO_2 has been developed as one of a visible light-responsible photocatalysts, although these doped-type photocatalysts remain a major subject due to structural stability.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)^{4,5)} is one of a novel photocatalyst which is responsible for visible light due to the 2.7 eV ($\lambda=450$ nm) of the band-gap (Scheme 1). The $\text{g-C}_3\text{N}_4$ can be responsible to water splitting (from 2 H_2O to 2 H_2 and O_2) under visible light irradiation⁶⁾, and therefore, the $\text{g-C}_3\text{N}_4$ has recently become a typical visible light-responsive photocatalyst with high physicochemical stability. Because the $\text{g-C}_3\text{N}_4$ is a metal-free organic material, it is not expensive driven from easy processes on preparation. Various compounds such as urea ($\text{CH}_4\text{N}_2\text{O}$), cyanamide (CH_2N_2), dicyandiamide ($\text{C}_2\text{H}_4\text{N}_4$), melamine ($\text{C}_3\text{H}_6\text{N}_6$), etc. are available as a precursor, and several physicochemical types of $\text{g-C}_3\text{N}_4$ (or $(-\text{C}_3\text{N}_4)$) can be prepared by heat treatment⁷⁾. As shown in Scheme 2, the $\text{g-C}_3\text{N}_4$ has a multilayered structure like the graphite while the specific surface area on $\text{g-C}_3\text{N}_4$ is generally lower than that of graphite. As a subject on C_3N_4 , inhibition of recombination on photo-generated electron-hole pair is an important point for enhancement of photocatalytic activity. Many workers have been pointed out that high exciton binding energy (ca. 0.2 eV) and low photoinduced carrier separation will inhibit the enhancement of high photocatalytic activity⁴⁾. Therefore, further improvement to control the photocatalytic properties by using the effective physicochemical techniques is called for to overcome the problems described above.



Scheme. 1 Schematic band-edge energy diagrams of TiO_2 (anatase) and C_3N_4 (graphitic).



Scheme. 2 Structure of layered $\text{g-C}_3\text{N}_4$.

In the present study, photocatalytic activity of several C_3N_4 -type photocatalysts were employed for VOC removal under living environment. For $\text{C}_3\text{N}_4 + \text{TiO}_2$ binary photocatalysts, binding effect of a semiconductor heterojunction between C_3N_4 and TiO_2 can be expected to suppress the recombination rate of charge carriers. Under irradiation of mercury lamp (UV + VIS) or LED light (VIS only) in a conventional fixed-bed photoreaction, the photocatalytic activity was evaluated by oxidative decomposition of HCHO (as a typical VOC with a harmful compound) with water vapor in flowing air at room temperature.

2. Experimental

The C₃N₄-based photocatalysts were prepared by using a cyanamide (NH₂CN) precursor in all the catalyst samples. Bare C₃N₄ was obtained by heat-treating of cyanamide powder in gas flow Ar, NH₃(20%)-N₂, or air; 60 mL/min in each gas) at 623 K for 6 hours, and then followed by washing with water or HCl(1M) solution, filtering, drying, and re-treated in Ar flow (60 mL/min) at 623 K for 6 hours. For combined photocatalysts between TiO₂ and C₃N₄, mechanically mixed C₃N₄+TiO₂ samples (TiO₂/C₃N₄=1–4 as weight ratio) were obtained by mixing the NH₂CN (as an equivalent weight in C₃N₄) and TiO₂ (P-25, Degussa) powders, and followed by a similar process to those of C₃N₄.

Photocatalytic activity was evaluated by using a fixed bed flow type photoreactor in atmospheric pressure. Each photocatalyst sample (50 mg) is set into a column cell made of quartz (30 mm in diameter, 10 mm in height) connected with inlet/outlet tube (4 mm i.d.), and the sample was exposed to O₂(21%)-N₂ flow (as dry air, 30.0 mL/min) with steam of vaporized aqueous formaldehyde solution (hold at 303 K: containing 200 ppm HCHO with <50 ppm CH₃OH mixed as a formaldehyde stabilizer) for 60 min at room temperature with air-cooling. Then the photocatalytic reaction was started by irradiation of each light source under flowing of HCHO-

H₂O, and reacted gaseous products were analyzed periodically by online TCD-GC (GC-14B, Shimadzu) with Porapak-T column. Before irradiation, the compounds in gas phase detected by TCD-GC are N₂, O₂, H₂O, HCHO, and CH₃OH. After irradiation, only a CO₂ product (without CO) was analyzed as a new compound. As a light source in this study, 250 W mercury lamp (H2.5TCIA41, Iwasaki Electric Co.) or 44 W white LED light (LED44E39, GE Lighting) were used. The illuminance in UV (at *ca.* 365 nm) region is 237 and 0 mW cm⁻² in mercury lamp and LED, respectively. The illuminance in VIS (visible light at *ca.* 560 nm) region is 13.7 and 23.5 mW cm⁻² in mercury lamp and LED, respectively. Spectral distribution (in VIS region) from these light sources are shown in Fig. 1, which were measured by using a Sekonic C-800 spectrometer.

3. Results and Discussion

Fig. 2 shows the X-ray diffraction pattern of C₃N₄ samples prepared in the present study. It is certain that high crystallinity of g-C₃N₄ can be obtained by calcination of NH₂CN in NH₃-N₂ atmosphere at 623 K, while the crystallinity decreased by washing with water or HCl solution. Because the crystallinity of g-C₃N₄ strongly relates to the photocatalytic activity⁸⁾, the characteristics of C₃N₄ should avoid changing during a reaction. As a subject on C₃N₄ photocatalysts utilized with water, both structural changes during the photoreaction and competitive adsorption between reactants and the water vapor (*e.g.*, HCHO and H₂O, in this study) should be important to evaluate the availability over the photocatalysts. As shown in Fig. 2, NH₂CN precursor remains with g-C₃N₄ in the samples after calcination in NH₃-N₂ or air. After calcination in NH₃-N₂, only a g-C₃N₄ phase was detected by washing with water or HCl solution. After calcination in air, washing with HCl solution needs to remove the remained NH₂CN precursor. In contrast, the g-C₃N₄ sample with slight NH₂CN precursor can be obtained after calcination in Ar atmosphere. In this sample, the XRD pattern due to g-C₃N₄ is almost kept on after

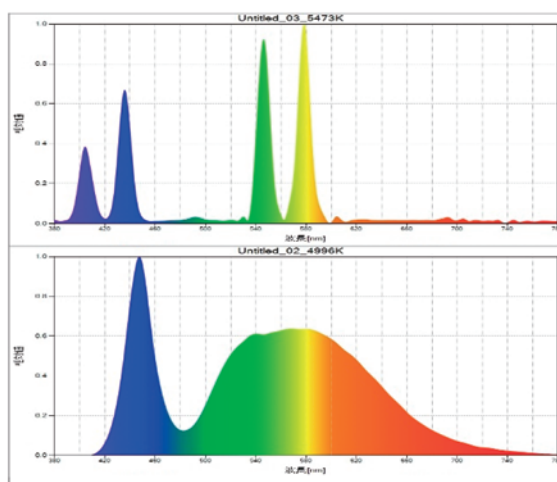


Fig. 1 Spectral distribution in VIS region (380–780 nm) from the light sources, mercury lamp and LED used in this study.

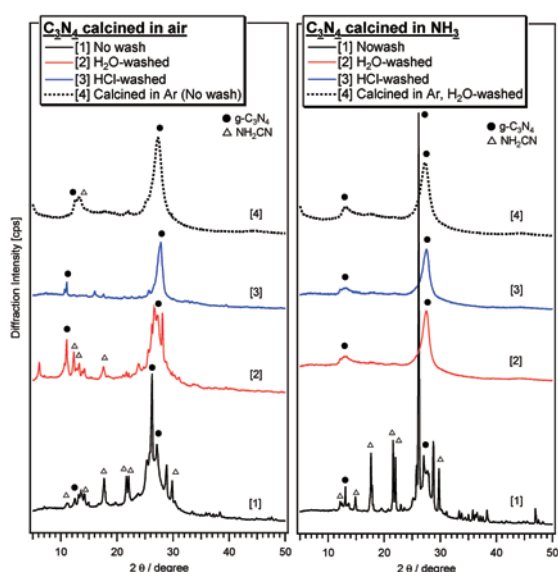


Fig. 2 XRD pattern of prepared C_3N_4 photocatalysts by heat-treatment in air (left hand) or ammonia (right hand), and then followed by washing with water or HCl(1M) solution.

washing with water. The effect of H_2O is possibly an important factor to obtain a durable photoactivity for oxidative VOC decomposition in the presence of water vapor, and therefore, it is summarized that appropriate preparation of g- C_3N_4 is available by calcination of NH_2CN in Ar flow at because of structural tolerance for water.

Diffuse reflectance UV-VIS spectra over the C_3N_4 samples prepared under various conditions are shown in Fig. 3. A shoulder peak at around 459 nm (due to 2.7 eV as typical band-gap energy for C_3N_4) should be necessary for absorption by the visible light in the C_3N_4 photocatalysts. The C_3N_4 sample calcined in NH_3 - N_2 before/after washing with H_2O or HCl solution, the shoulder peak appears distinctly. In case of the samples calcined in air, the absorption in VIS region (at ca. 459 nm) is unclear. In contrast, the VIS absorption is definitive in the C_3N_4 samples after calcination in Ar. These results suggest the difference of band-gap formation in VIS region by the variation of the calcined atmosphere for C_3N_4 preparation. To clarify the details, deconvolution of the UV-VIS spectra over the several C_3N_4 samples was introduced to analyze the formation of the important band in VIS region (1.5-4.0 eV). As

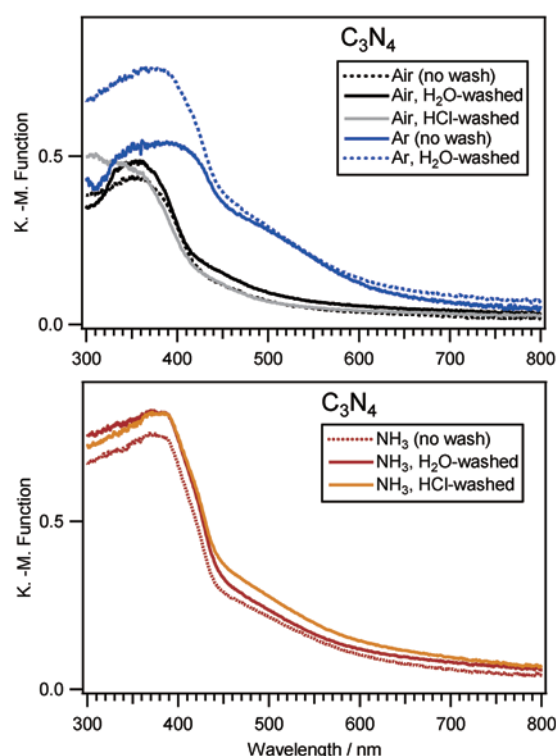


Fig. 3 Diffuse reflectance UV-VIS spectra of prepared C_3N_4 photocatalysts by heat-treatment in air, Ar (top) or ammonia (bottom), and followed by washing with water or HCl(1M) solution.

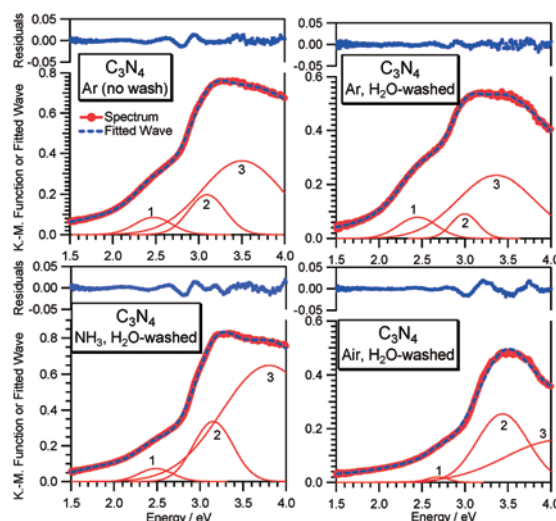


Fig. 4 Deconvolution of the UV-VIS spectrum on C_3N_4 samples by using three Gaussian waves. Each x-axis is indicated as energy (eV).

shown in Fig. 4 and Table 1, a peak component centered at 2.46-2.47 eV is indicated in the C_3N_4 samples calcined in Ar before/after washing with H_2O . It is noteworthy that the high ratio of this

Table. 1 Fitted parameters (by using three Gaussian waves) by deconvolution of the UV-VIS spectrum on C₃N₄ samples; shown in Fig. 4.

Ar (without washing)				Ar, H ₂ O-washed			
	Peak 1	Peak 2	Peak 3		Peak 1	Peak 2	Peak 3
<i>E</i> /eV	2.47	3.10	3.50	<i>E</i> /eV	2.46	2.99	3.37
Width	0.306	0.302	0.659	Width	0.318	0.225	0.613
Amp.	0.085	0.198	0.363	Amp.	0.081	0.098	0.219
Area(%)	8.0	18.4	73.6	Area(%)	14.1	12.1	73.7

NH ₃ , H ₂ O-washed				Air, H ₂ O-washed			
	Peak 1	Peak 2	Peak 3		Peak 1	Peak 2	Peak 3
<i>E</i> /eV	2.49	3.15	3.80	<i>E</i> /eV	2.68	3.44	4.08
Width	0.280	0.326	0.775	Width	0.181	0.420	0.861
Amp.	0.073	0.336	0.649	Amp.	0.020	0.255	0.157
Area(%)	3.2	17.3	79.5	Area(%)	1.5	43.6	55.0

absorption peak (to the total absorption) is exhibited, since this component of the absorption peak correlates with photoactivity in VIS irradiation. In the sample calcined in NH₃-N₂ after H₂O-washing, the peak appears at the same position (2.49 eV) although the relative ratio of absorption decreases in comparison with the sample calcined in Ar. For the sample calcined in air after H₂O-washing, only a weak absorbing peak strength of the VIS region (at 2.68 eV) can be seen. It is suggested that C₃N₄ calcined in Ar can be expected to possess the photocatalytic activity in VIS region because of definite VIS absorption even after H₂O-washing.

The photocatalytic activity under irradiation of mercury lamp (contains UV + VIS) over C₃N₄ catalysts, which were washed by water or HCl(1M) solutions before heat-treatment, is shown in Fig. 5. In brief, TiO₂ (P-25) shows the highest activity with no deactivation. The C₃N₄ photocatalyst (without washing) calcined in NH₃-N₂ show high activity in early stage of the reaction, but significant deactivation proceeds over the reaction time. The C₃N₄ photocatalyst calcined in air show lower activity than that calcined in NH₃-N₂. For these C₃N₄ photocatalysts, low photoactivity was brought about by washing with H₂O or HCl solution. In contrast, the C₃N₄ calcined in Ar

shows relatively higher photoactivity than in NH₃-N₂, and the activity was almost kept on even after washing with water. This result suggests the correlation between the photocatalytic activity and formation of metastable g-C₃N₄ structure (by XRD) and band structure in VIS region (by UV-VIS spectroscopy), and strong water resistance may inhibit the structural changes during the photoreaction. From these results, the following evaluation of photocatalytic activity by visible light (using LED light source) was carried out using C₃N₄ catalysts calcined in air after H₂O-washing.

The photocatalytic activity under LED irradiation over C₃N₄-based catalysts, which were washed by water, is shown in Fig. 6. TiO₂ (P-25) shows low activity in the initial reaction time, and then deactivation is noticeable. For P-25 TiO₂, photocatalytic activity has been reported under irradiation of visible light⁹⁻¹⁰⁾ although the activity is low and unstable. In brief, the photoactivity on TiO₂ is lower than that of C₃N₄ under LED irradiation which does not contain UV light. For bare C₃N₄ (calcined in Ar, after washing with H₂O) the photocatalytic activity in the initial step (for 10 min.) is very high, and the activity is almost as same as that in mercury lamp (UV + VIS) irradiation. But the deactivation cannot be

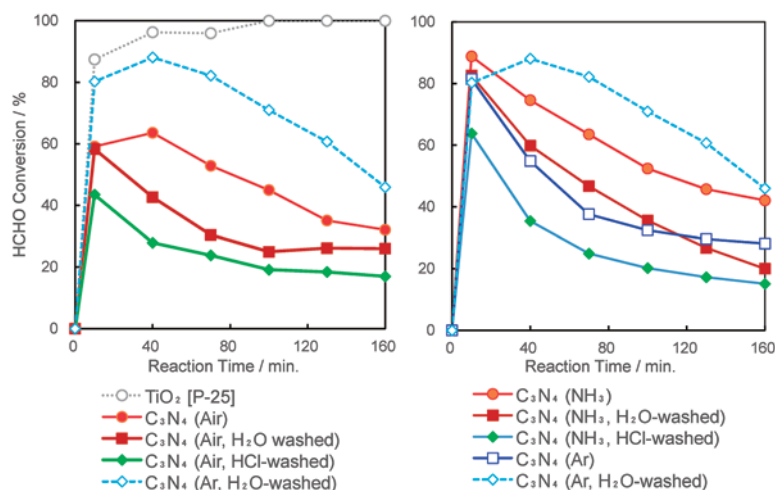


Fig. 5 Photocatalytic activity for HCHO decomposition with water vapor under irradiation of mercury lamp over C_3N_4 photocatalysts prepared by calcination in air (left), Ar (left/right), or NH_3 (right) before/after washing with H_2O or HCl solution.

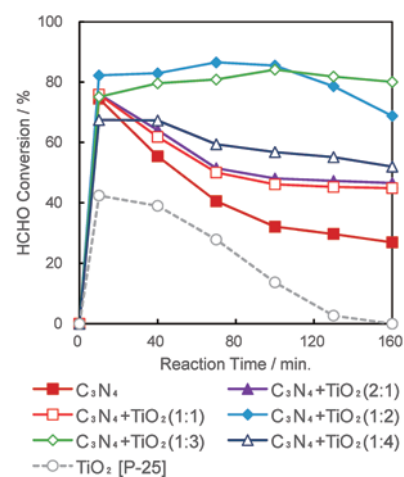


Fig. 6 Photocatalytic activity for HCHO decomposition with water vapor under LED irradiation over C_3N_4 photocatalysts prepared by calcination of $NH_2CN + TiO_2$ (P-25) mixture in Ar after H_2O -washing.

avoided over the time, which may be caused by a competitive adsorption between HCHO and H_2O . To overcome the deactivation with high photoactivity, $C_3N_4 + TiO_2$ composite catalysts were investigated because of an intention of forming a composite band. As shown in Fig. 6, high and durable photocatalytic activity can be obtained in $C_3N_4/TiO_2 = 1/2-1/3$ (as weight ratio). It is noteworthy that mixing effect between TiO_2 and C_3N_4 can expect the high photoactivity. We are now in the process of investigating the conditions and clarifying the controllable factors for durable and high photocatalytic activity under VIS irradiation.

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