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Preparation of a semiconductive compound obtained by the pyrolysis of urea under N_2 and the photocatalytic property under visible light irradiation

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ABSTRACT

Preparation and photocatalytic property of a compound prepared from the pyrolysis of urea under N_2 atmosphere was investigated. The compounds prepared over 773 K showed photo-absorption below 460 nm and the property of n-type semiconductor. The platinized compounds showed the photocatalytic activity on H_2 production from aqueous methanol under the visible light irradiation (shorter than 440 nm). The photocatalytic active phase was confirmed to be graphitic C_3N_4 (g-C_3N_4) like phase produced under the pyrolysis of urea above 723 K. The effects of the addition of cyanuric acid and melamine, regarded as the intermediates of the compounds to the photocatalytic activity were examined.

1. Introduction

Photocatalysts have extensively applied to various significant reactions. In most cases, oxide semiconductors, such as TiO_2, have widely employed as photocatalysts [1]. In order to develop effective photocatalysts, various modifications of oxide photocatalysts have been mainly carried out by doping anion and cation to improve the photoresponse and photocatalytic performance [2–12]. Beside the modification of conventional oxide photocatalysts, the development of new photocatalysts is expecting. The new expecting photocatalysts require well photoresponse and photocatalytic performance as well as the chemical stability under the photocatalytic reaction. Although various semiconductive materials can become the candidates as new photocatalyst systems, carbon based semiconductive compounds are the promising candidate for its stability and the photoresponse under visible light irradiation. In the typical case, Wang and Maeda et al. reported the photocatalytic property of graphitic C_3N_4 (g-C_3N_4) under visible light irradiation [13–15].

On the other hands, a number of studies have been carried out to improve the photoresponse of TiO_2 photocatalyst by the doping of nitrogen [2–7]. Urea has been applied as one of the effective nitrogen sources. Recently, Mitoraj and Kisch [16] reported that the generation of visible light response arose from the formation of s-triazine compounds containing melem and melone unit over the TiO_2 surface. This expresses that the compounds obtained by the pyrolysis of urea on TiO_2 played the significant role for generating the visible light response. However, few studies are concerning on the photocatalytic property of the compounds obtained by the pyrolysis of urea itself.

Previously, we found out that the production of semiconducting material prepared by the thermal condensation of urea under N_2 atmosphere [17]. The prepared material exhibited photo-absorption below 460 nm, photo-emission at 485 nm and photocatalytic activity of H_2 production from aqueous methanol under the irradiation. However, the detail investigations on this material have not been investigated so far.

In this study, we investigate the photocatalytic property of the semiconducting compounds prepared from urea. Here we report that the preparation, the characterization and the photocatalytic property of the compounds obtained from the pyrolysis of urea under N_2 atmosphere.

2. Experimental

2.1. Preparation of photocatalyst

The preparation of photocatalysts used in this study was carried out in a schlenk type test tube made of quartz under 1 atmospheric N_2 flow. Urea or the mixture of urea and its derivatives were introduced in the test tube. The pyrolysis of urea started after well exchanging the atmosphere into N_2 and was performed at prescribed temperatures for 2 h. The residue remained in the test tube after the pyrolysis was the compound applied to photocatalyst. Platinum was used as co-catalyst and platinum loaded photocatalyst was prepared by photodeposition method. The photodeposition method was carried out by dissolving the prescribed amount of H_2PtCl_6 in the reactant solution. Pt is

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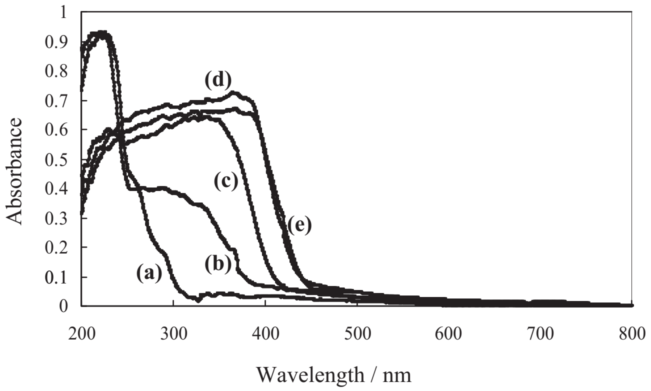

Fig. 1. UV–Vis spectra of the compounds prepared by the pyrolysis of urea at (a) 573 K, (b) 623 K, (c) 673 K, (d) 773 K and (e) 823 K.

deposited over the photocatalyst surface in the initial stage of the reaction.

2.2. Photocatalytic reaction

Photocatalytic reaction was carried out in a photoreaction cell, made of pyrex glass connected with iso-volumetric closed gas circulation system equipped with vacuum line and gaschromatograph sample inlet. The photocatalytic performance of the prepared compound was evaluated by photocatalytic H_2 production from aqueous methanol, where the reaction was one of the typical photocatalytic reactions and often applied as test reaction to evaluate the photocatalytic performance. The photocatalyst (0.5 g) was suspended in well out-gassed aqueous methanol (30 vol%, 100 ml) and then irradiation from Xe lamp (300 W) started. The wavelength of the irradiated wavelength was controlled by inserting high-pass cut off filters in the irradiation path. The evolved gas was collected in a sampling tube in the system and then analyzed by on line gas chromatograph.

2.3. Characterization

The prepared photocatalysts were characterized by UV–Vis spectroscopy, elemental analysis, and infrared spectroscopy. The semiconducting property was evaluated by measuring the photocurrent of the prepared photocatalyst. The measurements of photocurrent were carried out with three electrodes in an aqueous solution of 0.25 M Na_2SO_4 involving 50 vol% ethanol. The aqueous solution was purged by N_2 gas for 30 min prior to measurements. Platinum and Ag/AgCl were used as auxiliary and reference electrodes, respectively. Working electrodes were prepared by spreading a paste of the photocatalyst with water onto the ITO-glass ($10\,\Omega\,cm^{-2}$) and drying the surface in air. The potential change for the film electrode was measured with a Potentiostat/galvanostat under various irradiations.

3. Results and discussion

3.1. Photo-electrochemical property of the compound prepared by pyrolysis of urea under N_2

The photoelectrochemical property of the compounds prepared by the pyrolysis of urea was examined. Fig. 1 shows UV–Vis spectra of the compounds prepared at various temperatures. As shown in Fig. 1, the UV absorption band below 300 nm is observed in the spectrum of the compound prepared below 573 K, while a band at longer wavelength generates in the spectra of the compounds prepared over 623 K and the absorption edge shifts up to 460 nm with increasing the preparation temperature (as shown in Fig 1(b)–(e)). From the results in Fig. 1, semiconductive compounds are suggested to produce by the pyrolysis of urea over 623 K from the generation of UV–Vis absorption at longer wavelength. Particularly, the spectra of the compounds, prepared over 773 K, show the absorption edge in the visible light region at 460 nm (as shown in Fig. 1(e) and (f)). Then, the electrochemical measurement was performed on the compound prepared at 773 K.

From the electrochemical measurement, it was confirmed that positive photocurrent generated when the working electrode was irradiated by the Xe lamp where the irradiated wavelength was cut off up to 440 nm. The result of electrochemical measurement shows that the compound prepared from urea in this study has the property of n-type semiconductor and generating the photocurrent under visible light irradiation ($\lambda < 460$ nm). The results are expected that the compound exhibit the photocatalytic activity under visible light irradiation. Accordingly, the compound was applied as photocatalyst.

3.2. Photocatalytic behaviour of the compound prepared by pyrolysis of urea under N_2

Fig. 2 shows the photocatalytic evolution of H_2 from aqueous methanol in time over platinized (Pt (0.3 wt%)) urea derived compound prepared at 773 K under various irradiations, where the wavelength of the irradiations was controlled by inserting cut off filters in the irradiation path and the kinds of irradiation are expressed as the cut of wavelength of the filters. The preferable amounts of Pt cocatalyst were examined under the full arc of Xe lamp ($\lambda > 320$ nm) and the value was 0.3 wt% in this photocatalytic reaction system. As shown in Fig. 2, it is observed that H_2 produced constantly under various irradiations, and the photocatalytic H_2 production can be confirmed up to the wavelength cut off below 440 nm. Beside the production of H_2, no products such as N_2 and CO, were detected under the photocatalytic reaction. The photocatalytic activity is defined the amount of produced H_2 per hour.

These results indicate that the compound prepared by the pyrolysis of urea exhibits the photocatalytic activity on H_2 production from aqueous methanol when co-catalyst, such as platinum is combined. The photocatalytic activity decreases with the cut off wavelength, where the activities are 92 μmol/h under the irradiation of full arc, 62 μmol/h under the irradiation over 380 nm, 12 μmol/h under the irradiation over 420 nm and 3.0 μmol/h under the irradiation over 440 nm. The dependency of the photocatalytic activity on the cut off wavelength is agreement with the photo-absorption behavior shown in Fig. 1(d). It is notice that the photocatalytic reaction proceeds under the irradiation of visible light ($\lambda > 440$ nm). Then, the attention is paid to the photocatalytic activity under visible light irradiation.

Fig. 3 shows the photocatalytic activity of the compounds under the full arc and visible light ($\lambda > 420$ nm) irradiation from the Xe lamp as a function of the preparation temperature. As shown in Fig. 3, the photocatalytic activity increase with the preparation temperature and the photocatalyst prepared at 773 K show the maximum activity under the visible light and at 873 K under full arc irradiations. From the results in Figs. 1 and 3, the photocatalytic active phase generates in the compound prepared over 623 K and the compound prepared over 773 K starts exhibiting the photocatalytic activity under visible light irradiation. From these results, it is confirmed that the generation of photocatalytic activity under visible light irradiation is originated with shift of photo-absorption edge to visible light region accompanied with the growth of photocatalytic active phase by increasing the preparation temperature. The decreases of the photocatalytic activity of the compounds prepared at highly temperatures are probably originated with the formation of defect by the thermally decomposition of the pho-

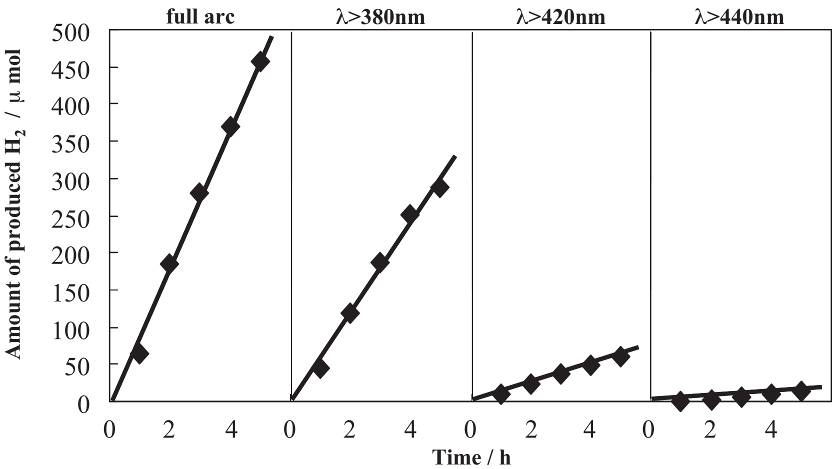

Fig. 2. Evolution of H_2 in time over the platinized (0.3 wt%) compound prepared by pyrolysis of urea under various irradiations, where the irradiations are controlled by inserting high-pass filter in the irradiation path.

tocatalytic active phase. Then, the detail examination is carried out on the structure of photocatalyst.

3.3. *Characterization of the prepared photocatalysts*

The elemental analysis was carried out. From the result, the composition of the elements was observed to be as the ratio of C, N, O, and H from 3:3:2:1 to 2:1:2:1. This result shows that the prepared compound consists of carbon, nitrogen, oxygen and hydrogen. Then, the detail states of the photocatalysts were examined by infrared spectroscopy.

Fig. 4 shows infrared spectra of the compounds prepared by the pyrolysis of urea at various temperatures. From Fig. 4, the infrared bands at around 3200 cm^{-1} and below 1800 cm^{-1} attributable to the compounds are observed. From the examination of the infrared spectra of urea and urea derivatives, the bands in Fig 4(a), corresponding to the compound prepared at 573 K, agree with those in the spectrum of cyanuric acid. This means that the urea condensed under N_2 atmosphere to form cyanuric acid like compound at 573 K. Fig. 4(b) and (c) shows the spectra of the compounds prepared at 623 K and 673 K, respectively. From the spectra in Fig. 4(a)–(c), it is notice that the shapes of the bands, in particular the spectral region below 1800 cm^{-1}, change with the preparation temperatures. Compared with the spectra among Fig. 4 (a)–(c), the intensity of band at 1734 cm^{-1}, which can be assigned to ν(C=O) of cyanuric acid, decrease with temperatures. Instead of the decrease of the intensity of the band at 1734 cm^{-1}, the intensity of the band at around 1610 cm^{-1} increased accompanied with changing the band shape at around 1450 cm^{-1}. These bands are similar with the spectrum of melamine in the region between 1700 cm^{-1} and 1300 cm^{-1}. These suggest that the bands in Fig. 4(c) are probably attributed to the vibrations of conjugated triazine ring. From these results, conjugated triazine ring forms in the compounds with increasing the preparation temperatures.

Fig. 4(d) and (e) shows the infrared spectra of the compound prepared at 773 K and 823 K, respectively. The spectra in Fig. 4(d) and (e) show the nearly the same shapes and these results suggest that the compound prepared over 773 K have nearly the same states. Compared with the spectra of Fig. 4(c) and (d), several new bands below 1400 cm^{-1} are clearly observed in Fig. 4(d). The generated new bands have been assigned to the vibration mode of melen or melon structure [16] and the shapes of the spectrum of Fig. 4(d) is similar with that of graphitic carbon nitride (g-C_3N_4) referred to previous reports [16,18]. Generally, g-C_3N_4 phase is reported to synthesize by the thermal condensation of cyanamide by way of melamine and no oxygen contains in the compounds [18]. Although the compound prepared by the pyrolysis of urea is confirmed to contain oxygen originated with urea from the results of the elemental analysis in this study, the result in Fig. 4 suggests that rearrangement of atoms in the compound probably occur by the pyrolysis of urea over 723 K to form g-C_3N_4 like species containing melen or melon structure. However, the details of the formation

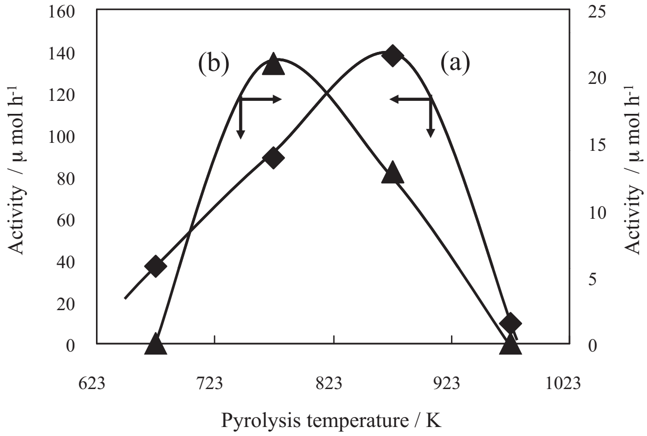

Fig. 3. The photocatalytic activity of the compounds prepared by the pyrolysis of urea under the irradiation of (a) full arc from Xe lamp and (b) visible light (λ > 420 nm) as a function of the preparation temperature.

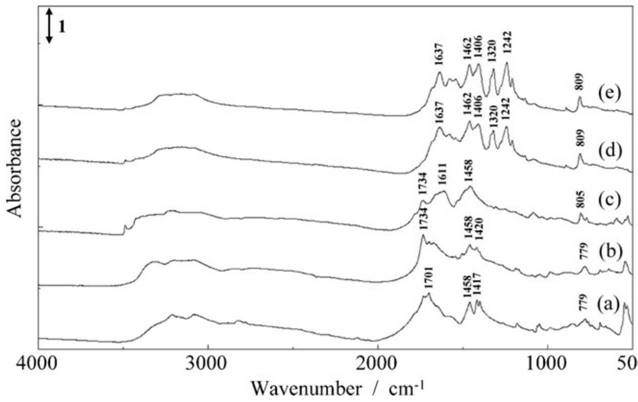

Fig. 4. Infrared spectra of the compounds prepared by the pyrolysis of urea at (a) 573 K, (b) 673 K, (c) 723 K, (d) 773 K and (e) 823 K.

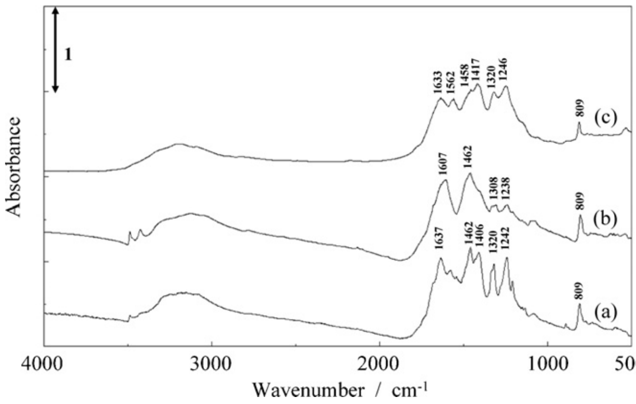

Fig. 5. Infrared spectra of the compounds prepared by the pyrolysis of (a) urea, (b) melamine and (c) cyanuric acid at 773 K.

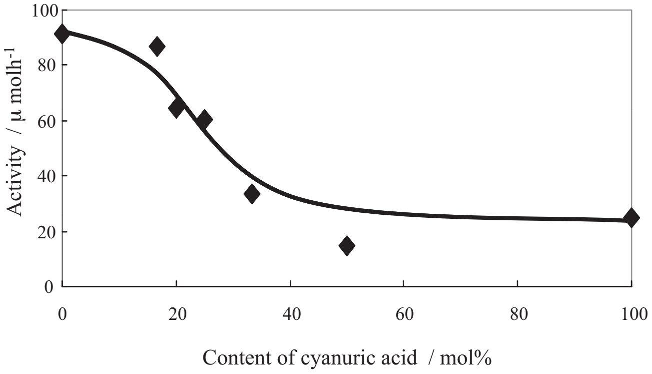

Fig. 6. Effect of cyanuric acid addition in the starting material of urea to the photocatalytic activity of the compound prepared at 773 K.

and the characters of g-C_3N_4 like compounds cannot be referred further in the present experimental condition.

From the results in Fig. 4, the compounds prepared from the pyrolysis of urea in this study was summarized as follows; urea condensed to mainly cyanuric acid up to 573 K, the cyanuric acid changes to a compound including conjugated triazin ring up to 723 K and the formation of g-C_3N_4 like compound by thermal reconstruction of atoms above 723 K.

From the results in Figs. 3 and 4, the photocatalytic activity noticeably improved, particularly under visible light irradiation, with the formation of g-C_3N_4 like species. From the previous studies of g-C_3N_4 prepared from various materials, the material showed the photocatalytic activity on the same reaction [13–15]. Therefore, the formation of g-C_3N_4 like species is important for the generation of photocatalytic activity.

The results in Figs. 3 and 4 also suggest that the g-C_3N_4 like species, the photocatalytic active phase, produces from urea by way of cyanuric acid like species. As mentioned above, g-C_3N_4 produced from cyanamide by way of melamine [18]. These suggest that cyanuric acid and melamine are regarded as the intermediates of photocatalytic active phase. Then the compounds prepared by the pyrolysis of cyanuric acid and melamine and the effect of the addition of them in the starting material of urea on the photocatalytic property were examined.

3.4. Photocatalytic property of the compound prepared from urea with the intermediates

The characters of the compounds prepared by the pyrolysis of cyanuric acid and melamine at 773 K were examined. From the results of UV–Vis spectra of the compounds originated with cyanuric acid and melamine, both of the spectra showed the same band as the spectrum of the compound prepared from urea as shown in Fig. 1(e).

Fig. 5 shows the infrared spectra of the compound prepared by the pyrolysis of (a) urea, (b) melamine and (c) cyanuric acid under N_2 at 773 K. As shown in Fig. 5, nearly the same spectra are observed as the compounds prepared from urea, cyanuric acid and melamine at 773 K. However, the difference can be observed in the detailed shapes of the spectra. In the spectra of the compound prepared from melamine at 773 K (Fig. 5(b)), the intensity of the bands attributed to melem or melon structure is weak compared with those in the spectra of the compound from urea (Fig. 5(a)). From previous works [18,19] concerning the formation g-C_3N_4 from cyanamide and melamine, g-C_3N_4 prepared by way of melamine but the preparation temperature was higher (over 823 K) than the condition in this study. This is probably the reason why the intensity of the bands is weak in Fig. 5(b). The spectrum of the compound prepared from cyanuric acid at 773 K gives nearly the same spectrum as the compound prepared from urea as shown in Fig. 5(a). However, the bands in the spectrum in Fig. 5(c) are much broader than that in Fig. 5(a). These mean that the same kind of compound produced from cyanuruic acid but the state is different from the compound prepared from urea. Then the effects of the addition of cyanuruic acid and melamine in the starting material of urea to the photocatalytic activity of the prepared compound were examined.

Fig. 6 shows the effects of the addition of cyanuric acid in the starting material of urea on the photocatalytic activity of the compounds prepared at 773 K under the irradiation of full arc of the Xe lamp. As shown in Fig. 6, the compound prepared from cynanuric acid at 773 K show the photocatalytic activity but the activity is noticeably lower than that prepared from urea. It is also observed that the photocatalytic activity decrease with increasing the content of cyanuric acid in the starting material. In particular, the compound prepared from the starting material, in which the content of cyanuric acid is 50%, shows the same activity as that prepared from pure cyanuric acid. These results suggest that the addition cyanuruic acid do not influence effectively to improve the photocatalytic performance.

Fig. 7 shows the effects of the addition of melamine in the starting material in urea on the photocatalytic activity of the compound prepared at 773 K under the irradiation of full arc from the Xe lamp. As shown in Fig. 7, the photocatalytic activity improves by the addition of melamine. The preferable content of melamine in the starting material is 25 mol%. The photocatalytic activity of the compounds decreases with the content of melamine more than 25 mol% in the starting materials. The dependency of the photocatalytic activity on the content of melamine in the starting material is different from that of cyanuric acid. It is notice that the addition of melamine gives positive effect to improve the photo-

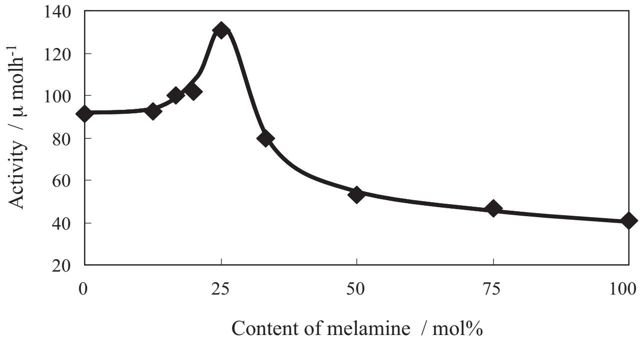

Fig. 7. Effect of melamine addition in the starting material of urea to the photocatalytic activity of the compound prepared at 773 K.

catalytic performance. In the previous papers [18,19], melamine is reported to be a path of the production of g-C_3N_4, which is regarded as active center of photocatalyst in this study, from the thermal condensation of cyanamide. In this study, the added melamine probably forms a core for the photocatalytic active center under the formation of the compound. The improvement of the photocatalytic activity was probably caused by the effective formation of the photoactive phase as g-C_3N_4 like structure by the addition of melamine. Since higher temperature is necessary to produce the phase by melamine itself as mentioned above, the photocatalytic activity decreases at the starting material with the high content of melamine.

4. Conclusion

In this study, we investigated the preparation and photocatalytic property of the compounds prepared by the pyrolysis of urea and urea derivatives under N_2 atmosphere and following conclusions were obtained.

(1) A semiconductive compound generates by the pyrolysis of urea over 623 K. Particularly, the compound prepared over 773 K shows the UV–Vis absorption in visible light region ($\lambda < 460$ nm) and positive photo-current detected up to the cut off the wavelength shorter than 440 nm. These indicate that the compound is n-type semiconductor and can generate the photocurrent under visible light irradiation.

(2) The compound shows photocatalytic activity of H_2 production from aqueous methanol when Pt is combined as co-catalyst. The photocatalytic activity is confirmed under visible light irradiation ($\lambda < 440$ nm). The compound prepared at 773 K shows the maximum photocatalytic activity under visible light irradiation.

(3) The composition of elements in the compound is confirmed at the ratio of C, N, O and H from 3:3:2:1 to 2:1:2:1. From infrared spectra of the compounds prepared at various temperatures, urea condensed to cyanuric acid below 573 K, and conjugated triazin ring forms up to 723 K and the atoms in the compounds re-constructs to form g-C_3N_4 like structure including melen ring above 723 K. The g-C_3N_4 like compounds regarded as the active compound of photocatalyst.

(4) The effects of the addition of cyanuric acid and melamine, which regards as intermediates under the pyrolysis of urea, in the starting material were examined to the photocatalytic activity. The addition of melamine is effective. This is probably caused by the effective formation of the photoactive phase as g-C_3N_4 like structure.

Acknowledgement

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