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Photodegradation of pollutant pesticide by oxidized graphitic carbon nitride catalysts

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ABSTRACT

Oxygen-doped graphitic carbon nitride (Og-CN) was synthesized by H_2O_2 -treating of graphitic carbon nitride (g-CN), which was prepared by the condensation-polymerization of melamine and the exfoliation. The successful oxidation was confirmed by the decrease of photoluminescence intensity, the detection of oxygen-including bond and the slight increase of surface area. Og-CN was applied to the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid in the aqueous phase under the UV and visible light irradiation and compared with the catalytic behavior of g-CN. The degradation efficiency of Og-CN was shipler than that of g-CN, the UV light irradiation was more effective than the visible light irradiation, and Og-CN was stable in three photocatalytic cycles with only 4% decrease. The kinetics analysis indicated that the photoreactions of both Og-CN and g-CN follow the zerothorder reaction rather than the first-order reaction. On the photoreaction mechanism study, the active species-trapping experiment, which was performed using 2,2,6,6-tetramethyl-1-piperdinyloxy free radical, t-BuOH and K1 for scavenging O_2^- , $O^\circ H$ and h⁺, respectively, confirmed the reactivity order of $O_2^{\bullet} > {}^{\bullet}OH > h^+$. Then the present research refers that Og-CN is a promising photocatalyst because it has extremely high total organic carbon removal (88 % of degraded 2,4-D after 120 min).

1. Introduction

Environmental pollutions by organic and organometallic compounds are drastically rising and becoming a serious problem from time to time all around the world [1–3]. This rapidly increased issue may be attributed to industrialization, urbanization and agricultural expansion. Specifically, the recent attention is that along with the intense agricultural demand, the amount of pesticides and/or herbicides administrated in agricultural works remarkably increases and it is a strong risk to human health [4,5]. Among organic chlorine pesticides, the most common one is 2,4-dichlorophenoxyacetic acid (2,4-D), which is used in the whole world, specifically, in the developing countries [6,7]. It is a non-biodegradable aromatic herbicide utilized to damage broad leaves from weeds, and thus its residue may admix in soil-borne and water bodies and becomes the environmental hazard. The World Health Organization classifies 2,4-D as a mildly toxic chemical and the maximum tolerable amount in drinking water is 100 ppb [8-10]. Thus, the development of appropriate treatments is necessary to maintain this condition. Among many treatments, filtration, adsorption, coagulation, and ion exchange methods have been explored to remove 2,4-D from water systems [11,12]. However, those treatments should be forced the resumption of 2,4-D and/or provide excess secondary chemical pollutants that can affect the environments.

Photocatalytic degradation is a more promising technique, because it actively uses renewable solar energy to change harmful pollutants to harmless products without using other oxidative chemicals [13,14]. In these cases, metal oxide or metal semiconductor catalysts have generally been used, although they are less abundant and toxic in some cases [15, 16]. Graphitic carbon nitride (g-CN) is a metal-free material consisting of the most abundant elements (carbon and nitrogen) and easily synthesized by the condensation polymerization of nitrogen-rich compounds such as thiourea, urea, cyanamide, dicyandiamide and melamine [17–19]. It is one of the most promising photocatalysts because of its stability, non-toxicity, tunability, reusability, flexible layer formability and small bandgap (about 2.7 eV) [20,21]. However, it suffers the recombination of charge carriers, the low visible

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https://doi.org/10.1016/j.jphotochem.2020.112955 Received 20 August 2020; Accepted 25 September 2020 Available online 28 September 2020 1010-6030/© 2020 Elsevier B.V. All rights reserved. light-harvesting ability and hence the low photocatalytic efficiency [22]. Recently it has been reported that when g-CN is hydrothermally introduced oxygen, it makes the product (oxygen-doped g-CN: Og-CN), which is expected to be derived more amount of pores, increased the electron mobility, decreased the charge recombination and enhanced the visible light responsibility [23–26].

In this work, g-CN was synthesized by the thermal condensation polymerization of melamine and followed by the hydrothermal-treating with H_2O_2 . The produced oxygen-doped catalyst (Og-CN) was compared to g-CN on their characteristics. The photocatalytic degradation of 2,4-D on the Og-CN catalyst utilizing ultraviolet (UV) and visible light sources was evaluated under the spectrophotometric analysis and compared with that on the g-CN catalyst. The kinetics analysis of the 2,4-D degradation was also performed, and the active species of the reaction was assessed by the trapping experiments. This research will clarify the effective photoreaction activity on Og-CN superior to g-CN and the degradation mechanism of 2,4-D.

2. Experimental

2.1. Reagents and instruments

All chemicals were of analytical grade reagents and used without further purification. Rhodamine 6 G (Rh 6 G), 2,4-dichlorophenoxyacetic acid (2,4-D, 99+ %), melamine powder (99 %), tert-butyl alcohol (99.5 %), potassium iodide, hydrogen peroxide solution (35 wt%) and 2,2,6,6-tetramethyl-1-piperdinyloxy free radical (TEMPO) (98+ %) were purchased from Across Organics (New Jersey, USA). Ultrapure water (resistivity: 18.2 M Ω cm⁻¹) was used throughout this work for the preparation of solutions.

Characterization of materials was done by a Fourier transform infrared (FTIR) absorption spectrophotometer (NICOLET 6700, Thermo Scientific, USA), a UV–vis absorption spectrophotometer (JASCO V-670 and BAS SEC2000, Japan) at a scan speed of 200 nm/min, a transmission electron microscope (TEM, JEOL, JEM-2000FXII, Japan) operating at a 200 kV accelerated voltage, Field-emission scanning electron microscopy (FESEM) JSM 6500 F FE-SEM (JEOL, Tokyo, Japan), and a photoluminescence (PL) spectroscope (F-7000, Hitachi High-Technologies Co., Japan). The X-ray diffraction was recoded on a diffractometer (Bruker, D₂ phaser, Germany) at $5-70^{\circ}$ using Cu k α radiation (1.54 Å) at 40 kV and 30 mA, the nitrogen adsorption-desorption isotherm experiment was done at 77 K using a Brunauer-Emmett-Teller (BET) surface area analyzer (BELSORB Max, Japan), the X-ray photoelectron spectroscopic (XPS) measurement was performed on a VG scientific, Model ESCALAB 250, England, a Zahner Zennium Electrochemical workstation (Germany), a Vario TOC select analyzer (Merit Science Corporation, Germany), and the ultrasonic processor (Q700, Misonix, USA) Equipped with a half-inch tip was used for homogenizing.

2.2. Syntheses of photocatalysts

The bulk graphitic carbon nitride was prepared by means of the condensation polymerization of melamine according to the previously reported method [25]. Briefly, melamine powder (7.5 g) was calcined in a ceramic crucible for 4 h at 550 °C in the air atmosphere, and the yellow powder product (bulk graphitic carbon nitride) was collected. The sheet-structured g-CN was prepared by the ultrasonication treatment of the bulk graphitic carbon nitride [27]. Typically, the aqueous dispersion (100 mL) of bulk graphitic carbon nitride (0.2 g) was homogenized for 5 h with an output voltage of 48 W in an ice bath, and the product (g-CN) was filtrated on a $0.2 \,\mu$ m cellulose membrane, washed three times alternately with water and ethanol, and dried overnight at room temperature.

Oxygen-doped graphitic carbon nitride (Og-CN) was synthesized by the solvothermal method [25,28]. Here, g-CN (0.1 g) was dispersed in different percentages of H_2O_2 (10, 20 and 30 %, 60 mL) and stirred for 30 min in water bath at 25 $^{\circ}$ C, and the dispersion was heated for 4 h at 120 $^{\circ}$ C in a Teflon-lined stainless autoclave. The solid product was filtrated and washed several times with water.

2.3. Quantum yield and photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid

The fluorescence quantum yields, QY, of two catalysts were calculated by Eq. 1 [29].

$$QY_x = \left(\frac{A_s}{A_x}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 QY_s \tag{1}$$

where A is the absorbance of a UV–vis absorption band, F is an area emission intensity, and n is a refractive index of solvent. Subscripts, s and x, refer to the standard and catalyst. Rhodamine B with a quantum yield of 0.31 was used as a standard.

For the photocatalysis experiment, photocatalyst (g-CN or Og-CN, 15.0 mg, 0.060 mg/mL) was mixed with an aqueous 2,4-D solution (100 ppm, 25.0 mL). An aqueous 2,4-D solution without photocatalyst was also prepared for the blank experiment. The photocatalytic degradation was performed under the UV light irradiation with a 250 W Hg lamp (HOYA-SCHOT EX250 UV light source, JAPAN SERVO Co., Ltd, Japan) or the visible light irradiation (a blue light laser, SEC 2000-DH light source, Japan) at room temperature. The distance of the light source from the surface of the solution was maintained 16 cm for the UV light source, and the visible light source was held at the 1 cm distance to the solution. After the catalyst was dispersed in the analyte solution, the reaction dispersion was constantly stirred for 30 min at the dark condition. When the light was turned on, the reaction time was defined as zero.

The concentration of 2,4-D in a reaction dispersion sampled at the 20 min interval was analyzed using an absorbance of a 283 nm absorption band of 2,4-D and a corresponding calibration curve (Supporting information Fig S1). The absorption spectra of the reaction solutions under the UV light and visible light source irradiations were recorded on a JASCO V-670 spectrophotometer with a 2 mm path length cuvette cell and on a UV-vis spectrometer (SEC 2000, BAS Inc.) with a 10 mm path length cuvette cell, respectively. The total organic carbon (TOC) contents were calculated as % TOC removal by (TOC0-TOC1)/TOC0x100, where TOC_0 and TOC_t are total organic carbon content before degradation and after degradation at certain time t, respectively. The degradation efficiency was calculated as the degradation ratio or the percent degradation between the initial absorbance of 2,4-D at 283 nm and the corresponding absorbance at a certain reaction time t. For every data, triplicate measurements were averaged. The degradation experiment using the photocatalyst was also applied to Rh6 G dye for comparison.

For active species-trapping (scavenging) experiments, trapping reagent (TEMPO, KI, or t-BuOH, 10 mM, 1 mL) was added to an aqueous 2,4-D solution and the photodegradation experiments were performed.

2.4. Optical properties of the materials

In order to estimate the bandgap of the materials, a Tauc's Eq. 2 was used.

$$\alpha h \upsilon = c \left(h \upsilon - Eg \right)^n \tag{2}$$

where Eg is a bandgap energy, α is an absorption coefficient, hv is an energy absorbed, and c and n are constants. In order to calculate the flat band potential, which is assumed to be the energy of the conduction band (E_{CB}) with respect to the energy of normal hydrogen electrode (NHE), a Mott-Schottky equation (Eq. 3) was applied by extrapolating the linear portion of the plot to the x- axis [30].

$$\frac{1}{C^2} = \left(\frac{2}{\varepsilon \varepsilon_0 A^2 e N D}\right) \left[V - \left(V_{fb} + \frac{KT}{e}\right) \right]$$
(3)

Journal of Photochemistry & Photobiology, A: Chemistry 404 (2021) 112955

Where C, ε , ε_0 , A, e, ND, V, V_{fb}, K, and T are the capacitance at the space charge region, the dielectric constant of the semiconductor, the permittivity of free space, the donor density (electron donor concentration for an n-type or hole acceptor concentration for p-type semiconductors), the applied potential, the flat band potential, the Boltzmann constant, and the temperature, respectively [30,31]. Then, Eg and E_{CB} (= V_{fb}) are obtained from the plots of α hv vs hv and C⁻² vs V plots, respectively.

3. Results and discussion

3.1. Characterization of photocatalysts

To assess the photocatalytic activities, the photocatalysts (g-CN and Og-CNs) were synthesized and characterized. As indicated in the TEM images (Fig. 1), both catalysts (g-CN and 2-Og-CN) represented the morphology where the sheet-like textures with amorphous shape are agglomerated. Similar TEM images of g-CN and 2-Og-CN have been reported [31]. The surface morphologies of pristine g-CN and oxidized 2-Og-CN were also visualized via FE-SEM. As depicted in Fig. 1B(a,b), the sheet like structures of the materials were observed. The elemental

compositions of carbon, nitrogen, and oxygen of g-CN and 2-Og-CN were determined from energy dispersive X-ray spectroscopy (EDS) analysis as shown in Fig. 1C(a,b). After the hydrothermal treatment of g-CN, the increment of oxygen (1.5%–6.8%) along with the decrease in atomic percentage of nitrogen (63.6–56.2%) indicates that some nitrogen atoms were replaced by oxygen atoms.

Then thermal heating of melamine molecules can produce the covalent organic framework consisting of heptazine unit as illustrated in Scheme 1, which was confirmed from N/C ratio > 1.5 obtained from EDS analysis [32]. The hydrothermal oxidation of g-CN generates the oxidized g-CN (Og-CN), where some nitrogen atoms in amine (C-NH_x (x = 1 or 2), C = N-C or N-C₃ bonds) will be replaced by oxygen to produce C—OH or C—O—C bonds (see Scheme 1) [31,33].

The FTIR absorption spectra of g-CN and Og-CNs are shown in Fig. 2A,B. A broad absorption band centered around 3300–3100 cm⁻¹ indicates the existence of an N—H stretching vibration band resulting from amine groups. Several bands at 1650–1200 cm⁻¹ correspond to the stretching modes of heterocyclic C—N bonds. Specifically, 1640, 1410, 1322 and 1250 cm⁻¹ bands are attributed to C=N, C–N, N-C₃ and NH-C₂ stretching vibration modes, respectively, of heptazine unit. A band at 810 cm⁻¹ is referred to the breathing mode (out of plane bending vibration mode) of heptazine units [34]. Additionally, after



Fig. 1. (A) HRTEM images, (B) FE-SEM images and (C) EDS analysis with inset atomic mass percentages of (a) g-CN and (b) 2-OgCN.



Heptazine

Scheme 1. Schematic illustration of reaction processes and their products on photocatalyst (g-CN and Og-CN) syntheses.

treating g-CN with different concentrations of H_2O_2 , a new peak at 1208 cm⁻¹ appeared (Fig. 2B), corresponding to the C-O-C stretching vibration mode [35], although C—OH bands were not clarified because of the less or overlapped contribution. Thus, IR spectra confirmed the existence of heptazine units in both semiconductors and oxidized units in the oxidized materials [35].

As seen in the UV–vis absorption spectra of g-CN and Og-CNs shown in Fig. 2C, the strong absorption band of g-CN was observed at 330 nm following shoulders around 230 and 400 nm, and a similar spectrum was observed even for Og-CNs. The influence of oxidation on the electronic property of g-CN was rather clarified on the PL spectra, where an emission band at 440 nm with a shoulder band around 460 nm was measured at the 275 nm excitation for both photocatalysts, as seen in Fig. 2D. Although the additional excitation bands were observed at 330, and 360 nm, the emission spectra at the 330 nm and 360 nm excitation generated relatively lower emission intensities at 440 nm, indicating that the main excitation band is at 275 nm. It should be noticed that the PL emission intensities of g-CN decreased after the oxidation, because the more electronegative oxygen atom effectively suppresses the recombination of the photo-generated electron-hole carriers (e^-/h^+) [31]. Additionally, there was a small red shift of an emission band as observed. This band shift is attributed to change in electronic structure after much doping the electronegative oxygen. The quantum yields of two catalysts were calculated by using Rhodamine B as a reference and obtained 14.8 % and 13.9 % for g-CN and 2-Og-CN, respectively, and those values are comparable with the reported values (12.5 %, 10.3 %) for graphitic carbon nitride-type semiconductors [36,37].

The XPS survey spectra, the XPS fine spectra with deconvolution and the lists of deconvoluted species of precursor (melamine) and two catalysts (g-CN and 2-Og-CN) are shown in Fig. 3 and Table 1. As seen in Fig. 3Aa, Ba and Ca, the former two compounds (melamine and g-CN) mainly consist of carbon and nitrogen elements but the intensity of oxygen element in 2-Og-CN increased because Og-CN is a product of oxidation reaction of g-CN. The deconvolution analysis of highresolution C 1s and N 1s spectra of melamine (Fig. 3Ab and 3Ac) displayed each two distinguishable peaks with binding energies at 285.7 and 288.9 eV (C 1s) and at 398.4 and 399.6 eV (N 1s). Based on these binding energies, the structural change was examined for the other two materials after polymerization and oxidation. The deconvoluted C 1s and N 1s spectra of g-CN (Fig. 3Bb and Bc) revealed additional peaks besides melamine-based bonds (C-NHx(x=1,2) and C=N-C). There are C 1s peaks at 283.1 and N 1s peak at 400.2 eV which was attributed to N-C3 in heptazine and additionally C 1s peaks at 287.2 eV corresponds to NHCO2/COH appeared for g-CN [38-42]. On 2-OgCN, although the same numbers of C 1s and N 1s peaks as those on g-CN were deconvoluted, the relative strengths of C 1s peaks varied: Melamine-based C 1s peaks became weaker and alternatively a new peak at 284.4 eV appeared (Fig. 3Cb). This variation can be attributed to the oxidation of C-NHx(x = 1,2), C = N-C or N-C₃ bond to C—O—C/COH bond [34–36]. The oxidation also influenced the N 1s peaks (Fig. 3Cc). Among three N 1s peaks of g-CN, the area intensity of a 398.1 eV peak especially decreased after the oxidation. Correspondingly, the O 1s spectrum of 2-Og-CN presented the C-O-C/COH peaks at 530.3 and 531.6 eV (Fig. 3Cd) [42]. Thus, it was proved from the analysis of XPS that the heptazine unit exists in g-CN and the oxidation of g-CN produces some oxidized COC/COH bonds as illustrated in Scheme 1.

The XRD patterns of g-CN, 1-Og-CN, 2-Og-CN and, 3-Og-CN are shown in Fig. 4A. The main peak at $2\theta = 27.95^{\circ}$ in g-CN is reported as a (002) plane of the lamellar structure and this plane can be attributed to the interplane distance of the stacked heptazine structures [40]. The d-spacing of this peak was evaluated to be 0.318 nm, and this peak showed the angle shift to $2\theta = 28.03^{\circ}$ or the d-spacing shift to 0.317 nm in Og-CN. Since this shift is negligibly small, it can be interpreted that the oxidation scarcely affected the interplane distance. The second peak observed at $2\theta = 13.45^{\circ}$ corresponding to the d-spacing of 0.663 nm is associated with (100) plane, but also assigned to be the (210) reflection of orthorhombic structure [43]. In any case, this peak angle of Og-CN did not vary from it of g-CN, indicating no in-plane structural variation between them. Thus, the XRD result confirmed that the crystal structure of g-CN was not influenced by the oxidation. The peaks of g-CN around 2Θ (35–40) can be assigned to uncondensed melamine structure, which may be fully condensed after hydrothermal treatment [44,45].

As indicated in Fig. 4B, the nitrogen adsorption-desorption curves of g-CN, 1-Og-CN, 2-Og-CN and, 3-Og-CN belong to the type IV isotherm with a hysteresis at high relative pressure, which indicates the mesoporous structure of these catalysts. The specific surface area, pore volume, and pore diameter of the catalysts were evaluated from these isotherms and Barrett, Joyner and Halenda (BJH) plots. The Og-CN(s) exhibited slightly larger specific surface area and pore volume, and



Fig. 2. (A) (B) FTIR absorption spectra (C) UV-vis absorption spectra and (D) PL spectra of g-CN and Og-CNs.



Fig. 3. (a) Survey XPS spectra of (A) melamine, (B) g-CN and (C) 2-Og-CN and their high resolution XPS spectra and deconvoluted peaks of (b) C 1s, (c) N 1s and (d) O 1s.

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XPS deconvoluted peaks and their assignments for g-CN and 2-OgCN [34,35,39-42].

Element	t Melamine		g-CN	g-CN			Assignment*	
	BE (eV)	Area intensity (a.u.)	BE (eV)	Area intensity (a.u.)	BE (eV)	Area intensity (a.u.)		
			283.1	166.5	284.4	470.9	^{b,c} CN ₃	
~ 1	285.5	344.5	285.7	554.7	285.5	444.3	a,b,c C-NHx(x = 1,2)	
CIS			287.2	236.9	287.7	241.6	^{b,c} NHCO ₂ / ^c C-O-C/COH	
	288.3	546.9	288.9	467.3	288.7	446.0	^{a,b,c} C=N-C	
	398.4	798.4	398.1	988.1	398.1	287.6	$^{a,b,c}C-NHx(x = 1,2)$	
N 1 s	399.6	1030.1	399.4	654.9	399.4	575.8	^{a,b,c} C=N-C	
			400.2	537.2	400.2	415.2	^{b,c} NC ₃	
					530.3	108.4	°C-O-C/OH	
O 1 s					531.6	614.3	°C-O-C/OH	
	532.5	329.6	532.3	501.5	532.9	466.4	^{a.b,c} NHCO ₂	
*	_	1						

Assignment to ^amelamine, ^bg-CN, and ^c2-OgCN.



Fig. 4. (A) XRD patterns and (B) nitrogen adsorption-desorption isotherms of g-CN and Og-CNs. Inset in (B) is their BJH pore-size distributions.

lesser pore diameter than g-CN as shown in Table 2. The results of nitrogen adsorption-desorption isotherms showed the increase in surface area and porosity (pore volume) with increase in oxygen content, although pore diameter decreased with oxygen content (Table 2 and Fig. 4 inset). The decrease of pore volume at highest oxygen content (3-Og-CN) as well as similarity of its surface area to 2-Og-CN may relate to the limitation of the oxygen content on photocatalytic activity as

Table 2
$\label{eq:constraint} Analyses \ of \ nitrogen \ adsorption-desorption \ is otherms.$

catalyst	specific surface area $(m^2 g^{-1})$	pore volume $(cm^2 g^{-1})$	pore diameter (nm)
g-CN	28.35	0.224	31.63
1-Og-	37.22	0.242	26.53
CN			
2-Og-	39.32	0.262	26.68
CN			
3-Og-	40.02	0.247	24.73
CN			

described above. Thus, increase in oxygen content increases the porosity and specific surface areas of the materials up to certain maximum limit. The values of the surface area obtained was comparable to the previously reported values for graphitic carbon nitride-type semiconductors [29]

It was confirmed from the characterizations described above that g-CN and Og-CNs were constructed from heptazine unit, and the oxidation of g-CN changed C—N=C group to ester group or terminal amine group to hydroxyl group. According to this chemical modification, Og-CNs lowered the quantum yield of PL emission and increased the surface area. These variations should influence the catalytic properties.

3.2. Photocatalytic degradation of 2,4-D by g-CN and Og-CN

The herbicide 2.4-D has two absorption bands at 230 and 283 nm, which correspond to the $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively, as seen in (Supporting information Fig S1). Photocatalytic degradation of 2,4-D by g-CN and 2-Og-CN was performed under the UV and visible light irradiations. Then the absorption spectra of 2,4-D at 283 nm decreased with the reaction time as seen in Figs. 5Aa,b, Ba,b and S2. The % degradation of 2,4-D by different catalysts under UV and visible light irradiations was plotted in Fig. 5Ac,Bc, which was calculated using the absorbance at 283 nm and also included the result of the degradation reaction of 2,4-D without catalyst under UV light irradiation. It should be noted that the slight degradation (about 20 % at 140 min irradiation) happened even without catalyst. This slight degradation can be explained by the absorption of energy from the UV light source, which produces the excited state (2,4-D*), leads the excited singlet state (¹2,4-D) and gives rise to the triplet state (³2,4-D) through the non-radiative transition [46].

The photocatalytic degradation of 2.4-D increased from g-CN and 1-Og-CN to 2-Og-CN but that of 3-Og-CN was almost similar to that of 2-Og-CN. As a result, 2-Og-CN was focused and analyzed in comparison to g-CN. As seen in Fig. 5Ac,Bc, the degradation of 2,4-D was accelerated in the presence of catalysts g-CN and 2-Og-CN under the photo irradiation and reached a maximum of 96.3 % and 98.7 % after 140 min under the UV light irradiation and 21.8 % and 61.5 % after 120 min under the visible light irradiation, respectively. The results indicate that the UV



Fig. 5. UV–vis absorption spectra of 2,4-D on photocatalytic degradation reaction process under (A) UV and (B) visible light irradiations by (a) catalyst g-CN and (b) catalyst 2-Og-CN. (c) The % degradation of 2,4-D as a function of reaction time for no catalyst, g-CN, 1-Og-CN, 2-Og-CN and 3-Og-CN under (A) UV and (B) visible light irradiations. (C) The % TOC removal after the degradation reaction of 2,4-D by g-CN and 2-Og-CN catalysts under UV light Source. (D) Recyclability examination by three successive degradations of 2,4-D on catalyst 2-Og-CN under UV light irradiation.

light source is remarkably effective superior to the visible light source and Og-CN is more active as a photocatalyst than g-CN.

TOC was selected as the mineralization index for the degradation products of 2,4-D and the time dependent TOC removal from 2,4-D solutions during the photoreaction under UV light source was displayed in Fig. 5C. The TOC removal rate reached highest percentage of 84.2 % at 120 min for 2-Og-CN catalyst but it for g-CN was 72.5 % at 120 min. These numerical values indicate that 77 and 88 % of degraded 2,4-D by g-CN and 2-Og-CN, respectively, were decomposed to become CO₂ and H₂O, as the photodegradation of 2.4-D was 94.5 and 95.6 % by g-CN and 2-Og-CN, respectively, after 120 min UV light irradiation. Thus, the 2-Og-CN catalyst is high in TOC removal rate compared to the g-CN catalyst and the catalysts have sufficiently better degree of mineralization for practical uses [47,48].

The recyclability is the prerequisite for the catalysts to be used in the practical application. As shown in Fig. 5D, the reusability was tested by using catalyst 2-Og-CN for three successive 2,4-D degradations under the UV light irradiation and over 94 % of the original photocatalytic

activity was retained, indicating the excellent photocatalytic recyclability of the 2-Og-CN. This decrease may be due to the photocorrosion [41].

3.3. Photocatalytic degradation kinetics

To analyze the kinetics of photocatalytic degradation of organic pollutants, the conventional Langmuir-Hinshelwood (L-H) model can be used, as indicated in Eq. 4 [49].

$$\frac{-dC}{dt} = \frac{kKC}{1+KC}$$
(4)

where C is the concentration of pollutant at a reaction time t and k and K are the photo-degradation rate constant and the adsorption constant, respectively. These equations can be simplified under some conditions. For KC>>1, Eq. 4 becomes Eq. 5 and can be expressed as Eq. 6 when integrated under the boundary condition of the initial concentration, C_0 , to the concentration, C_t , at the degradation time t. Then Eq. 6 is the

zeroth order kinetics equation.

$$-dC/dt = k$$
(5)

$$C_t - C_0 = -kt \text{ or } \frac{C_t}{C_0} = -\frac{k}{C_0}t + 1$$
 (6)

When KC << 1, Eq. 4 can be reduced to give an Eq. 7 and the integrated Eq. 8, which is the first order reaction.

$$-dC/dt = kKC$$
(7)

$$\ln(C_t/C_0) = -kKt \tag{8}$$

Based on the theoretical Equations described above, the % degradation vs time plot of selected catalysts (g-CN and 2-Og-CN) under both light sources in Fig. 5Ac,Bc was replotted to be the C_t/C_0 vs time plot. As seen in Fig. 6, the fitting or the linearity to the zeroth order type reaction equation was good. The degradation rate constant k and the variance R² values for different light sources and different catalysts are listed in Table 3 and the kinetics fittings are indicated in Fig. 6. The kinetics rate constants follow the order of 2-Og-CN (UV) > g-CN (UV) > 2-Og-CN (Vis) > g-CN (Vis) \approx no catalyst (UV) and the variances were always higher than 0.99. Separately, $ln(C_t/C_0)$ values were plotted as a function of reaction time following the first order Eq. 6. As seen in Fig S3 and Table S1, although the linearity of $\ln(C_t/C_0)$ against reaction time was found, the variance of the fitting linearity dissipated from 0.92 to 0.99 and was inferior to the fitting based on the zeroth order type reaction equation. Thus, it can be noted that the catalytic performance of 2-Og-CN was higher than that of g-CN, the UV light was more preferable than the visible light as an irradiation light source, and the reaction follows to the zeroth order kinetics equation.

Table 4 summarizes the degradation reports of 2,4-D using different catalysts [8,14,50-53]. Most of the previous reports were performed using metal oxide photocatalysts like TiO2 and ZnO except the ZnIn₂S₄/g-CN catalyst [49]. Although the present experiments confirmed that the irradiation of UV lamp is more effective than that of visible light and the other researches were also examined on UV light, the visible light also acted well on MoO₃/ZnO nanorod catalyst [54]. When the percent degradation and the reaction time were compared in association with the light intensity, catalyst dosage, and initial concentration of 2,4-D, it can be noted that even for highly degrading metal-based catalysts (MoO3/ZnO nanorod (99 %) and hydrothermal TiO₂ (96 %)) [50,52], the amount of the catalyst used was large in comparison with the present works. Additionally, with respect to %TOC



Fig. 6. Ct/Co plots of 2,4-D as a function of time for no catalyst under UV light irradiation and g-CN and 2-Og-CN under UV and visible light irradiations.

Table 3

Kinetics data obtaine	d from the fitting to tl	he zeroth order equation

Variable	No catalyst, UV	g-CN, Vis	2-Og-CN, Vis	g-CN, UV	2-Og-CN,. UV
k (ppm/ min)	0.00150	0.00194	0.00503	0.00854	0.00975
R ²	0.99977	0.99983	0.99808	0.99518	0.99025

removal the present catalysts g-CN and 2-Og-CN reached 72.5 % and 84.2 % respectively within 120 min and shows remarkably superior performance compared to reports in the Table. Besides, even if the initial concentration of 2,4-D was large in the present case, the reaction was accomplished at the similar time as the other reports. As a result, the present metal-free covalent-organic framework photocatalysts (g-CN and Og-CN) reacted similarly as or more effectively than inorganic metal-oxide-based photocatalysts.

The catalytic quality of two catalysts was evaluated even on the degradation of Rh 6 G dye. The excellent photo-degradation capacity of the two catalysts was also proved on the degradation of Rh 6 G dye: The dve was almost completely degraded within 20 min under the UV light irradiation (Fig S4). The result also showed the higher catalytic performance over the metal oxide-based catalysts because of a higher rate of degradation of Rh 6 G at the higher initial dye concentration by g-CN and Og-CN [55].

3.4. Mechanisms of photocatalytic reaction

In order to confirm the active species involved in the photocatalytic reaction, the active species-trapping experiment was performed. The photodegradation of organic substances assisted by photon-irradiated semiconductors results in the generation of electron/hole (e⁻/h⁺) pair, which may produce hydroxyl radical (*OH) and/or superoxide radical anion $(O_2^{\bullet-})$ capable to react with the active sites [52,53]. Therefore, the mechanism of photocatalytic degradation of 2,4-D can be interpreted based on the trapping process of active species. This examination was done by introducing TEMPO, t-BuOH and KI as effective scavengers for $O_2^{\bullet-}$, $^{\bullet}OH$, and h^+ , respectively, during the photodegradation [48]. As indicated in Fig. 7A, when the photodegradation of 2,4-D by 2-Og-CN under the UV light irradiation was performed in the presence of scavengers, all scavengers had a suppression effect on the degradation reaction of 2,4-D, and the degree of suppression decreased in the order of TEMPO > t-BuOH > KI. This result indicates that $O_2^{\bullet-}$ was more active and followed by ·OH and h⁺ in the participation of reaction. Thus, the effective scavengers scavenge active species generated from the photocatalysts and suppress the reaction of active species with 2,4-D. Then the proposed reaction mechanism by the active species and the final reaction products are indicated below, as described in Eqs. 9-12.

A plausible mechanism for the photocatalytic activities with respect to band gap and the separation of photo-generated electron-hole pairs was also proposed. The conduction band (CB) and valence band (VB) potentials was calculated from flat band of the Mott-Schottky plot (Fig. 7B), which is the x intercept of the linear portion for g-CN and 2-Og-CN were -0.72 and -0.78 eV vs NHE respectively as indicated in Fig. 7A. Similarly, the Eg values for selected 2-Og-CN is 2.70 and that of g-CN is 2.89 calculated from Tacu's plot (Fig. 7C). Based on the calculated Eg, ECB, and EVB the mechanistic diagram was indicated with respect to the redox potentials of the materials verses the NHE as indicated in Fig. 7D. Then the reaction mechanism can be illustrated in Fig. 7E.

Semiconductor (photocatalyst) + $hv \rightarrow e^{-}(Og-CN, CB) + h^{+}(Og-CN, VB)(9)$ $CN + OH^{-} + OH$

$$Og - CN + H_2O(adsorbed) \rightarrow Og - CN + OH^- + OH$$
 (10)

$$e^{-}(Og - CN, CB) + O_2 \rightarrow Og - CN + O_2^{\bullet -}$$
(11)

Table 4

Comparison of the catalytic degradation of 2,4-D.

Catalyst	Light Source	Catalyst Dosage (mg/ mL)	2,4-D Dosage (ppm)	Reaction Time (min)	% Degradation	%TOC removal	Reference
Nitrogen-doped TiO ₂	Visible light, 250 W	0.1(mg)	40	180	83	ND	[50]
Hydrothermal TiO ₂	UV lamp, 11 W	0.2	50	120	96	44	[52]
Pt/TiO ₂	Mercury lamp, 400 W, 365 nm	0.12	20	90	≥ 90	ND	[53]
Fe@ZrO ₂	UV lamp, 254 nm	1	50	150	60		[14]
MoO ₃ /ZnO nanorod	Visible light	1.5	20	120	99	23	[54]
Tourmaline-coated	UV lamp, 200–1000 W/m, 254	0.5	20	40	>90	ND	[8]
TiO ₂	nm						
ZnIn ₂ S ₄ /g-CN	Xe lamp, 500 W	0.02	100	180	90	41.6	[49]
gCN	Visible light	0.06		120	21	ND	Present
							Work
OgCN	Visible light	0.06	100	120	61	ND	Present
							Work
gCN	UV lamp, 4.5 W	0.06	100	140	97	72.5	Present
						(120 min)	Work
OgCN	UV lamp, 4.5 W	0.06	100	140	99	84.2	Present
						(120 min)	Work

ND: not detected.



Fig. 7. (A) The effects of scavengers (t-BuOH, TEMPO and KI) on the degradation of 2,4-D by 2-Og-CN under UV visible light irradiation, (B) Mott-Schottky plots of g-CN and 2-Og-CN, (C) Tauc's plots of g-CN and 2-Og-CN, (D) the band energy diagram with respect to NHE, and (E) the schematic illustration of the photodegradation on a catalyst Og-CN.

$$2.4 - D(O_2^{\bullet-}, \bullet OH \text{ or } h^+) \rightarrow Degradation product$$
 (12)

It was revealed that the higher degradation was observed on the UV light irradiation as compared to the visible light irradiation. This is ascribed to the higher threshold energy of UV ray as compared to the visible light source of the lower energy. The electronegative oxygen atom in Og-CN can effectively suppress the recombination of photogenerated electrons and holes which can also enhance the photocatalytic efficacy.

4. Conclusions

In this work, the photocatalytic degradation performance of Og-CN on 2,4-D pesticide with UV and visible light sources was reported and compared with that of g-CN. Because some amounts of oxygen were displaced the nitrogen atom in the g-CN, the surface area and PL properties of Og-CN varied from those of g-CN, and the photocatalytic degradation efficiency of 2,4-D increased compared to the g-CN

catalysts. The superoxide ion $(O_2^{\bullet-})$ species, which dominates in photocatalytic degradation of 2,4-D, should be generated more from oxidized material (Og-CN), and thus Og-CN becomes more effective on the photocatalytic performance than that of g-CN. The increment in the photocatalytic activity of Og-CN should also be attributed to the increase in electron mobility of elemental oxygen and the decrease in recombination rate, which can be improved after oxidation. As a result, Og-CN exerted the photocatalytic activity and, especially, its total organic carbon removal was remarkably high different from inorganic catalysts.

Because g-CN-based materials are metal-free, low toxic, and synthesized from most abundant materials, they are prospective photocatalysts as well as the semiconductor material. However, their low visible light responsiveness hinders its catalytic ability in visible light. Thus, to use g-CN-based materials as metal-free photocatalysts for reactions and to be applied as semiconductors for energy generation and storage, the demanding more research is requested in the improvement of the bandgap by hybridizing or doping other semiconductor materials.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 112955.

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S.Y. Ejeta and T. Imae

Journal of Photochemistry & Photobiology, A: Chemistry 404 (2021) 112955

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