

Article

Subscriber access provided by University of Virginia Libraries & VIVA (Virtual Library of Virginia)

Effects of Surface Defects on Photocatalytic H2O2 Production by Mesoporous Graphitic Carbon Nitride under Visible Light Irradiation

Yasuhiro Shiraishi, Yusuke Kofuji, Hirokatsu Sakamoto, Shunsuke Tanaka, Satoshi Ichikawa, and Takayuki Hirai

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.5b00408 • Publication Date (Web): 09 Apr 2015

Downloaded from http://pubs.acs.org on April 12, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Effects of Surface Defects on Photocatalytic H₂O₂ Production by Mesoporous Graphitic Carbon Nitride under Visible Light Irradiation

Yasuhiro Shiraishi,^{*,†,‡} Yusuke Kofuji,[†] Hirokatsu Sakamoto,[†] Shunsuke Tanaka,¹ Satoshi Ichikawa,[§] and Takayuki Hirai[†]

[†] Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

[‡] PRESTO, JST, Saitama 332-0012, Japan

| Department of Chemical, Energy and Environmental Engineering, Kansai University, Suita 564-8680, Japan

§ Institute for NanoScience Design, Osaka University, Toyonaka 560-8531, Japan

Supporting Information Placeholder

ABSTRACT: Photocatalytic production of hydrogen peroxide (H_2O_2) from ethanol (EtOH) and molecular oxygen (O_2) was carried out by visible light irradiation ($\lambda > 420$ nm) of mesoporous graphitic carbon nitride (GCN) catalysts with different surface areas, prepared by silica-templated thermal polymerization of cyanamide. On these catalysts, the photoformed positive hole oxidize EtOH, and the conduction band electrons localized at the 1,4-positions of the melem unit promote two-electron reduction of O_2 (H_2O_2 formation). The GCN catalysts with 56 and 160 m² g⁻¹ surface areas exhibit higher activity for H_2O_2 production than the catalyst prepared without silica template (surface area: 10 m² g⁻¹), but further increase in the surface area (228 m² g⁻¹) decreases the activity. In addition, the selectivity for H_2O_2 formation significantly decreases with an increase in the surface area. The mesoporous GCN with larger surface areas inherently contain a larger number of primary amine moieties at the surface of mesopores. These defects behave as the active sites for four-electron reduction of O_2 , thus decreasing the H_2O_2 selectivity. Furthermore, these defects also behave as the active sites for photocatalytic decomposition of the formed H_2O_2 . Consequently, the GCN catalysts with relatively large surface area but with small number of surface defects promote relatively efficient H_2O_2 formation.

KEYWORDS: Photocatalysis; Hydrogen peroxide; Graphitic carbon nitride, Visible light; Oxygen reduction

INTRODUCTION

Hydrogen peroxide (H_2O_2) is a versatile clean oxidant that emits only water as a byproduct and is widely used for pulp bleaching, disinfection, and organic synthesis.¹ H_2O_2 has also attracted much attention as a new energy carrier for fuel cells, alternative to H_2 , because it is water-soluble and can be used in an one-compartment cell for electricity generation.² H_2O_2 is currently manufactured in industry by the anthraquinone method that needs high-energy-consuming two-step oxidation and hydrogenation reactions on Pd-based catalysts.³ Recently, H_2O_2 synthesis with H_2 and O_2 has been studied extensively with Pd⁴ or Au–Pd bimetallic catalysts.⁵ This direct synthesis quantitatively produces H_2O_2 , but requires extreme care due to the potentially explosive nature of the H_2/O_2 mixed gases. A new catalytic process capable of producing H_2O_2 without H_2 is therefore desired.

Photocatalytic H₂O₂ production on semiconductor catalysts such as titanium dioxide (TiO₂) has also been studied.^{6–8} The reactions are carried out by UV irradiation (λ <400 nm) of an O₂-saturated water with catalyst in the presence of electron and proton donor such as alcohols. Photoexcitation of the catalyst produces the positive hole (h⁺) and electron (e⁻) pairs. The h^+ oxidize alcohol and produce aldehyde and H^+ (eq. 1), while the e^- promote two-electron reduction of O_2 and produce H_2O_2 (eq. 2).

$$R-CH_2OH + 2h^+ \rightarrow R-CHO + 2H^+$$
(1)

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

The reaction proceeds at ambient temperature without H_2 and is potentially a safe and sustainable H_2O_2 synthesis. Its efficiency is, however, very low since the selectivity for the amount of H_2O_2 formed relative to the amount of alcohol consumed is ~6%.⁹⁻¹¹ This is because one-electron reduction of O_2 [superoxide (*OOH) radical formation, eq. 3] and four-electron reduction of O_2 (water formation, eq. 4) occur predominantly on the catalysts. These suppress two-electron reduction of O_2 (eq. 2), resulting in very low H_2O_2 selectivity.

$$O_2 + H^+ + e^- \to \bullet OOH \tag{3}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}$$

Earlier, we found that graphitic carbon nitride (GCN), a metal-free polymeric semiconductor with a graphitic stacking

structure of melem sheets,^{12,13} promotes selective two-electron reduction of O₂ and efficiently produces H₂O₂.^{14,15} Visible light irradiation ($\lambda > 420$ nm) of GCN with a small surface area 10 m² g⁻¹ [GCN(10) catalyst], prepared by a simple thermal polymerization of cyanamide, ¹² produces H_2O_2 with ca. 90% selectivity. Raman spectroscopy, electron spin resonance (ESR), and *ab initio* calculation revealed that the selective two-electron reduction of O₂ is ascribed to the efficient formation of 1,4-endoperoxide species on the melem unit. As shown in Scheme 1, the photoformed e⁻ are localized at the 1,4-positions of melem unit (a). The e^{-} reduces O_2 and creates a superoxo radical (b). This is rapidly reduced by another e⁻ at the *para* position and produces 1,4-endoperoxide species (c), which is readily transformed to H₂O₂. The efficient formation of 1,4-endoperoxide $(b\rightarrow c)$ may suppresses one-electron reduction of O2 (OOH formation, eq. 3) and four-electron reduction of O₂ (water formation, eq. 4), thus promoting selective two-electron reduction of O_2 (eq. 2).



Scheme 1. Proposed mechanism for selective formation of H_2O_2 on the photoactivated GCN surface.

The purpose of the present work is to improve the catalytic activity of GCN while maintaining high H2O2 selectivity. It is well known that photocatalytic activity of semiconductor materials increases with an increase in their surface area.¹⁶ Some post synthesis methods for the surface area enlargement of GCN have been proposed such as exfoliation of melem sheets by thermal oxidation etching,¹⁹ ultrasonication,^{20,21} and scission of the parts of the C-N bonds by chemical or thermal treatments.^{22,23} More popular way is the direct synthesis of GCN with large surface areas. Several methods have been proposed such as creation of mesoporous GCN by thermal polymerization of different C, N-containing precursors such as urea, thiourea, and guanidine derivatives²⁴⁻²⁶ and creation of GCN nanowires, nanorods, or nanofibers by the treatment of melamine with HNO₃ followed by thermal polymerization.² The most simple and widely-accepted way is the creation of mesoporous GCN based on silica-templating method reported by Wang et al.^{30,31} They synthesized mesoporous GCN by thermal polymerization of cyanamide with silica particles (ca. 12 nm) as a template followed by removal of the particles by washing with base. This produces mesoporous GCN with very large surface area (up to 380 m² g⁻¹), which can easily be controlled by the amount of silica particles added. Several

literatures revealed that a variety of photoreactions such as H₂ evolution,^{30,31} alcohol oxidation,³² CO₂ reduction³³, radical polymerization,³⁴ air purification,²² and pollutant degradation³⁵ proceed efficiently on the mesoporous GCN with increased surface areas as compared to the nonporous GCN.

In the present work, we synthesized GCN(x) catalysts with different surfaces areas $[x (m^2 g^{-1}) = 56, 160, and 228]$ by the silica-templated polymerization of cyanamide^{30,31} and used them for photocatalytic H₂O₂ production with ethanol (EtOH) as an electron and proton donor under visible light irradiation $(\lambda > 420 \text{ nm})$. Similar photocatalytic system for alcohol oxidation on mesoporous GCN has already been reported by other group;³² however, there is no mention of H_2O_2 formation. In the present study, photocatalytic activity for "EtOH oxidation" increases with an increase in the surface area of the catalysts, as reported.³² We found that GCN(56) and (160) catalysts exhibit higher activity for "H₂O₂ formation" than nonporous GCN(10), but GCN(228) shows decreased activity. In addition, the selectivity for H₂O₂ formation significantly decreases on the catalysts with larger surface areas. ESR, X-ray photoelectron spectroscopy (XPS), electrochemical analysis, and *ab initio* calculation revealed that the catalysts with larger surface areas contain a larger number of primary amine moieties at the surface of mesopores. These surface defects behave as active sites for four-electron reduction of O₂ (eq. 4), thus decreasing the H_2O_2 selectivity. In addition, these defects also behave as active sites for reductive decomposition of the formed H₂O₂. Consequently, a GCN catalyst with a relatively large surface area but with a small number of surface defects promotes relatively efficient H₂O₂ formation.

RESULTS AND DISCUSSION

Preparation and characterization of catalysts

Nonporous GCN(10) catalyst was obtained by calcination of cyanamide at 823 K for 4 h under N_2 as yellow powders.¹² The respective mesoporous GCN(56), (160), and (228) catalysts were prepared according to literature procedure:³⁰ calcination of a mixture of cyanamide and different amounts of a Ludox HS40 solution containing ca. 12 nm silica particles under N_2 at 823 K for 4 h followed by washing with a 4 M NH₄HF₂ solution at 298 K for 24 h produced yellow powders of the catalysts.

Table 1 shows the properties of GCN catalysts. As shown in Figure S1 (Supporting Information), N₂ adsorption/desorption analysis of mesoporous GCN shows typical type-IV isotherm, although nonporous GCN(10) shows almost no hysteresis loop. As shown in Figure 1, transmission electron microscopy (TEM) images of GCN(228) clearly exhibit mesopores, indicating that the silica-templated polymerization indeed creates mesosphere pore structure.^{13,30} As shown in Figure S2 (Supporting Information), X-ray diffraction (XRD) patterns of the catalysts shows distinctive diffraction at $2\theta = 27.4$ (d = 0.325 nm), assigned to the (002) packing of melem sheets.^{12,13} In that, mesoporous GCN show lower peak intensity than the nonporous GCN(10) due to their low crystallinity by the polymerization with a silica template, as observed in the related system.³⁶ Figure S3 (Supporting Information) shows the diffuse reflectance UV-vis spectra of the catalysts. Mesoporous GCN show spectra similar to those of nonporous GCN at $\lambda > 420$ nm, but show stronger absorption at $\lambda < 420$ nm due to the multiple light scattering by the mesoporous structure.^{30,37} Tauc plot of the absorption data revealed that the

59 60 band gap energies of mesoporous GCN are very similar to those of the nonporous GCN (ca. 2.57–2.62 eV) regardless of the presence of mesopores.

Photocatalytic activity

Photocatalytic H2O2 production was carried out with EtOH as the electron and proton donor.¹⁴ An EtOH/water (9/1 v/v) mixture (5 mL) containing each respective catalyst (20 mg) was photoirradiated at $\lambda > 420$ nm by a Xe lamp with magnetic stirring under O₂ (1 atm) at 298 K. All of the systems produce CH₃CHO as the main oxidation product of EtOH with only minor amounts of CH₃COOH and CO₂, as is the case for nonporous GCN(10).¹⁴ Figure 2a shows the time-dependent change in the amount of CH₃CHO during photoreaction on the respective catalysts. The GCN catalysts with larger surface area exhibit higher activity for CH_3CHO formation, indicating that, as reported by several literatures,^{30–35} enlarged surface area of GCN indeed enhances photocatalytic cycles. Figure 2b shows the time profiles for H₂O₂ formation during the reaction. GCN(56) and (160) catalysts exhibit higher activity for H_2O_2 formation than GCN(10), but GCN(228) is ineffective. Figure 2c shows the time profiles for the selectivity of the amount of H₂O₂ formed relative to the amounts of oxidation products of EtOH {= $[H_2O_2]/[CH_3CHO + CH_3COOH + (CO_2)/2] \times 100$ }. In the case of GCN(10), as we reported earlier,¹⁴ the H_2O_2 selectivity at the early stage of reaction (3 h) is 92% and scarcely changes even after prolonged photoirradiation (~24 h). In contrast, the H₂O₂ selectivities on mesoporous GCN at 3 h are much lower and decrease with an increase in the surface area: 92% for GCN(10) > 72% for GCN(56) > 58% for GCN(160) > 42% for GCN(228). This clearly indicates that the selectivity for two-electron reduction of O₂ decreases with an increase in the surface area of catalysts.

Surface defects on the catalysts

The decrease in the H_2O_2 selectivity associated with an increase in the surface area of catalysts (Figure 2c) is ascribed to the formation of a large number of *primary amine moieties* on the surface of mesopores. As schematically shown in Scheme 2a, this originates from the polymerization of cyanamide at the silica surface. Acidic silica surface attracts the amine moieties of cyanamide molecules.³⁸ Thermal

Table 1. Properties of Respective Catalysts.

polymerization therefore creates primary amine moieties on the surface. Subsequent removal of silica by the dissolution with NH_4HF_2 therefore left these moieties on the surface of mesopores. These surface defects behave as the active sites for four-electron reduction of O_2 (water formation, eq. 4) and, hence, decrease the selectivity for two-electron reduction of O_2 on the 1,4-positions of melem units (H₂O₂ formation, eq. 2).



Figure 1. Typical TEM images of GCN(228) catalyst.

catalyst	$S_{\rm BET}^{a}$ / m ² g ⁻¹	$D_{\rm p}^{\ b}$ / nm	$V_{\rm p}^{\ c}$ / cm ³ g ⁻¹	E _{bg} ^d / eV	composition of N atoms ^e / %				
Catalyst					N _{pyridine}	N _{center}	N _{tertiary}	N _{secondary}	N _{primary}
GCN(10)	10	-	_	2.62	71.6	11.9	13.9	2.0	0.6
GCN(56)	56	15.4	0.18	2.61	70.3	11.7	12.2	3.9	1.9
GCN(160)	160	11.2	0.39	2.57	70.1	11.7	9.1	6.5	2.6
GCN(228)	228	9.9	0.54	2.59	70.7	11.8	5.4	8.1	4.0

^{*a*} Brunauer-Emmett-Teller (BET) surface area. ^{*b*} Barrett-Joyner-Halenda (BJH) adsorption pore size. ^{*c*} BJH adsorption pore volume. ^{*d*} Band gap energies determined by a plot of the Kubelka-Munk function versus the energy of light absorbed (Figure S3, Supporting Information). ^{*e*} Determined by integration of N1s XPS charts (Figure 3) and CO₂-TPD profiles (Figure 4).



Figure 2. Time-dependent change in the amounts of (a) CH₃CHO and (b) H₂O₂, and (c) H₂O₂ selectivity during photoreaction on the respective GCN(*x*) catalysts. Photoirradiation was carried out with a 2kW Xe lamp (light intensity at 420–500 nm was 26.9 W m⁻²). H₂O₂ selectivity (%) = [H₂O₂] / ([CH₃CHO] + [CH₃COOH] + [CO₂] / 2) × 100.



Scheme 2. (a) Proposed mechanism for the formation of surface defects on the walls of mesopores. (b) Different N atoms on GCN.

The formation of surface defects on the mesoporous GCN is confirmed by XPS analysis. Figure 3 show the XPS charts for N1s level of respective GCN catalysts. All of the charts can be deconvoluted into the three components. As reported³⁹ and as shown in Scheme 2b, these components are assigned to sp² hybridized N atoms of melem units (N_{pyridine}) at 398.7 eV (pink), trigonal N atoms of melem center (N_{center}) and tertiary amine N atoms (N_{tertiary}) of melem terminal at 400.2 eV (blue), and primary (N_{primary}) and secondary amine (N_{secondary}) N atoms of melem terminal at 401.3 eV (green). The respective charts clearly show that contribution of the green component (N_{primary} + N_{secondary}) increases with an increase in the surface area of catalysts. This suggests that, as shown in Scheme 2a, thermal polymerization of cyanamide in the presence of silica particles indeed creates a large number of primary and secondary amine moieties.

The formation of a large number of primary amine moieties on the GCN catalysts with larger surface areas is confirmed by temperature-programmed desorption (TPD) analysis with CO₂. Figure 4 shows the CO₂-TPD profiles for respective catalysts. All of the profiles can be deconvoluted into three desorption peaks, assigned to the CO₂ molecules desorbed from N_{pyridine} (174 °C, pink), N_{secondary} (224 °C, cyan), and N_{primary} sites (301 °C, purple), respectively.⁴⁰ The amount of CO₂ desorbed from the N_{primary} sites increases with an increase in the surface area of catalysts. This indicates that GCN with larger surface areas indeed possess larger number of N_{primary} sites. The composition of respective N atoms on the GCN catalysts (Scheme 2b) can be determined by the integration of the deconvoluted components on the XPS (Figure 3) and CO₂-TPD data (Figure 4) and are summarized in Table 1. The composition of primary amine moieties (N_{primary}) on the nonporous GCN(10) is only 0.6%, but the mesoporous GCN with larger surface area have larger number of N_{primary} [up to 4% for GCN(228)]. The results indicate that, as shown in Scheme 2a, primary amine moieties are indeed produced on the surface of mesoporous GCN catalysts.

Properties of one-electron reductions of O₂

The lower H_2O_2 selectivity on the mesoporous GCN is because they promote four-electron reduction of O_2 (water formation, as eq. 4). One-electron reduction of O_2 (*OOH radical formation, eq. 3) is not involved in the selectivity decrease. This is confirmed by ESR analysis with 5,5-dimethyl 1-pyrroline N-oxide (DMPO) as a spin trapping reagent. An EtOH/water (v/v 9/1) mixture (5 mL) was photoirradiated with respective GCN catalysts (20 mg) and DMPO (0.1 mmol). Figure 5 shows the ESR spectra of the solutions recovered after photoreaction for 3 min. All of the solutions exhibit distinctive signals assigned to the DMPO–[•]OOH spin adduct ($\alpha_N = 13.5$ G; $\alpha_H^{\beta}= 9.8$ G, g = 2.0067).^{14,41} The signal intensities on the respective catalysts are very similar, indicating that similar numbers of [•]OOH radicals are produced on these catalysts. The results suggest that one-electron reduction of O₂ (eq. 3) is not involved in the decreased H₂O₂ selectivity on the mesoporous GCN catalysts.



Figure 3. XPS charts for N₁s levels of GCN(x) catalysts. Black line is the obtained chart, and gray line is sum of the deconvoluted components. The respective components are represented in Scheme 2b.



Figure 4. CO_2 -TPD profiles for respective GCN(*x*) catalysts. Black line is the obtained profile, and gray line is sum of the deconvoluted components. The respective components are represented in Scheme 2b.



Figure 5. ESR spectra measured at 298 K for the solutions recovered after photoirradiation of respective GCN(x) catalysts in an EtOH/water/O₂ system. Photoirradiation was performed for 3 min under the conditions identical to those in Figure 2 with DMPO (0.1 mmol).

Properties of four-electron reduction of O₂

The lower H₂O₂ selectivity on mesoporous GCN is ascribed to the enhanced four-electron reduction of O₂. Electrochemical analysis with a rotating disk electrode confirms this. Figure 6a shows the linear sweep voltammograms of GCN(10) and (228) catalysts measured on a rotating disk electrode in a buffered aqueous solution (pH 7) under O₂ atmosphere at different rotating speed.^{42,43} The diagnostic Koutecky–Levich plots of the data obtained at the constant electrode potential (–0.4 V) are illustrated in Figure 6b, and the slope of the plots obtained by linear regression was used to estimate the average number of electrons (*n*) involved in the overall reduction of O₂.^{44,45} The plots were interpreted on the following equations, where *j* is the measured current density, *j*_k is the kinetic current density, and ω is the electrode rotating speed (rpm), respectively:

$$j^{-1} = j_k^{-1} + B^{-1} \omega^{-1/2}$$
(5)

$$B = 0.2nFv^{-1/6}CD^{2/3}$$
(6)

F is the Faraday constant (96485 C mol⁻¹), v is the kinetic viscosity of water (0.01 cm² s⁻¹), C is the bulk concentration of O_2 in solution (1.3 × 10⁻⁶ mol cm⁻³), and *D* is the diffusion coefficient of O_2 (2.7 × 10⁻⁵ cm² s⁻¹), respectively.⁴⁶ The j_k values obtained on the GCN(10) and GCN(228) catalysts determined by the intercept of the Koutecky-Levich plots are 0.79 and 1.19 mA cm⁻², respectively. The larger j_k value of GCN(228) indicates that O_2 is reduced more efficiently due to the larger surface area.⁴⁷ The n value for GCN(10), determined by the slope, is 2.07, indicating that the GCN catalyst with a small surface area indeed selectively promotes two-electron reduction of O_2 (n = 2).⁴⁸ This is consistent with high H₂O₂ selectivity (ca. 90%) obtained by photoreaction experiments (Figure 2c). In contrast, the n value for GCN(228) is 2.72, which is much larger than that of GCN(10). This indicates that the GCN catalyst with a larger surface area indeed promotes four-electron reduction of O_2 (n = 4). This is also consistent with the decreased H₂O₂ selectivity during photoreaction (Figure 2c).





Figure 6. (a) Linear-sweep voltammograms of GCN(10) and GCN (228) catalysts measured on a rotating disk electrode at different rotating speed. (b) The Koutecky–Levich plots of the data obtained at the constant electrode potential (-0.4 V).

Recently, Zheng et al.⁴⁹ performed electrochemical analysis for O₂ reduction on the mesoporous GCN with a large surface area (250 m² g⁻¹), prepared by thermal polymerization of cyanamide in the presence of a SBA-15 mesoporous silica as a template followed by the removal of template by washing with NH₄HF₂. This material also exhibits a large *n* value (2.6), similar to that obtained in the present study. This supports the enhanced four-electron reduction of O₂ on GCN with a large surface area. The change in multi-electron reduction properties of O₂ is associated reasonably well with an increase in the number of primary amine moieties (N_{primary}) on the GCN catalysts. These findings therefore imply that these defects sites may contribute to the enhanced four-electron reduction of O₂.

Photoreduction properties of the surface defects

As shown in Scheme 1, conduction band electrons formed on the nonporous GCN catalyst with a small surface area are localized at the 1,4-positions of the melem unit. They reduce O_2 and rapidly produce 1,4-endoperoxide species, which is readily transformed to H_2O_2 . This thus promotes selective two-electron reduction of O2.14 In contrast, on the mesoporous GCN catalysts with larger surface areas, a large number of primary amine moieties on the melem terminal behave as the active sites for four-electron reduction of O₂. This results in decreased H₂O₂ selectivity. This is confirmed by ab initio calculations of the conjugated melem models (Figure 7) based on the time-dependent density functional theory (TD-DFT), performed within the Gaussian 03 program. The electronic transitions of all of the single, double, and triple melem models are mainly contributed by HOMO \rightarrow LUMO (S₀ \rightarrow S_1) transitions. Interfacial plots for the respective orbitals are summarized in Figure 7. The electrons on HOMO for the double and triple melem models are located at the 2,6-positions of the melem unit. This suggests that these nitrogen atoms on the melem units behave as the oxidation sites, as is the case for single melem model.¹

In the case of single melem model (a), as we reported earlier,¹⁵ the LUMO electrons are located at the 1,4-positions of the melem. This suggests that conduction band electrons are indeed localized on these atoms, and they behave as the sites for two-electron reduction of O₂. In this case, LUMO electrons are also located at the terminal primary amine moiety. This indicates that conduction band electrons are also localized on these sites, and they also behave as the reduction sites. In the case of double melem model (b), LUMO electrons are also located at the 1,4-positions of melem and the terminal primary amine moieties. In this case, the secondary amine moiety situated between two melem moieties does not possess electron distribution. This suggests that the secondary amine moiety does not act as the reduction sites. In the case of triple melem model (c), LUMO electrons are also not located at the tertiary amine moiety. The above facts involving (i) large distribution of LUMO electrons onto the primary amine moieties, and (ii) the decrease in H2O2 selectivity with an increase in the amount of primary amine moiety, strongly suggest that the primary amine moieties on the surface of mesopores behave as the active sites for four-electron reduction of O2. As a result of this, GCN catalysts with larger surface area exhibits decreased H2O2 selectivity.

Photocatalytic decomposition of H₂O₂

As shown in Figure 2c, during the photocatalytic H_2O_2 production, the H_2O_2 selectivity obtained on the GCN(10) catalyst scarcely changes even after prolonged irradiation (ca. 90%). In contrast, the H_2O_2 selectivity on the mesoporous GCN catalysts decreases with the irradiation time, and the decrease is more apparent for the catalysts with larger surface areas. The results clearly indicate that the mesoporous GCN with larger surface areas promote subsequent decomposition of the formed H_2O_2 . Stirring the H_2O_2 solutions in the dark condition with respective catalysts or under photoirradiation without catalyst under N_2 atmosphere scarcely changes the H_2O_2 amount. This suggests that H_2O_2 is photocatalytically decomposed on the mesoporous GCN. As reported for several semiconductor photocatalytic systems,^{44,50} H_2O_2 is reductively decomposed by the donation of conduction band electrons as follows:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{7}$$

4

5

6

7

8

9

10

11

16 17

18 19

20 21

22

23 24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60



Figure 7. Interfacial plots of main orbitals for (a) single, (b) double, and (c) triple melem-conjugated models, calculated at the DFT level (B₃LYP/6-₃IG(d)).

The GCN(10) catalyst (20 mg) was added to an EtOH/water mixture (9/1 v/v, 5 mL) with 200 μ mol H₂O₂ and photoirradiated (λ >420 nm) under N₂ atmosphere. As shown in Figure S4 (Supporting Information), photoirradiation leads to a decrease in the H_2O_2 amount. As shown in Table 1, the GCN(10) catalyst contains very small amount of primary amine moieties. This indicates that the 1,4-positions of the melem unit behave as the active sites for photocatalytic decomposition of H₂O₂ (eq. 7). However, as shown in Figure 2c, H_2O_2 selectivity on the GCN(10) catalyst scarcely changes even after prolonged photoirradiation. This means that, during photoirradiation with O₂, the 1,4-positions of melem units predominantly reduces O_2 and scarcely decomposes H_2O_2 . The significant decrease in the H₂O₂ selectivity with time on the mesoporous GCN catalysts is therefore probably due to the photocatalytic decomposition of H₂O₂ on the primary amine moieties. On these sites, basic primary amine moieties^{51,52} attract the acidic H₂O₂ molecules. This may promote rapid H₂O₂ decomposition on the mesoporous GCN catalysts with larger surface areas.

CONCLUSION

Mesoporous GCN prepared by thermal polymerization of cyanamide with silica nanoparticles as a template followed by removal of the particles were used for photocatalytic H₂O₂ production from EtOH and O₂ in water under irradiation of visible light. The GCN catalysts with larger surface areas inherently contain a larger number of primary amine moieties on the surface of mesopores. Selectivity for H₂O₂ formation via two-electron reduction of O₂ by the conduction band electrons localized on the 1,4-positions of the melem unit decreases with an increase in the surface area. This is because the primary amine moieties behave as the active sites for four-electron reduction of O₂. These basic primary amine sites also behave as the sites for reductive decomposition of the formed H₂O₂, probably due to the strong interaction with acidic H₂O₂. The obtained results suggest that creation of GCN catalysts with a large surface area but with a smaller number

of primary amine moieties is very important for efficient photocatalytic $\rm H_2O_2$ production.

EXPERIMENTAL SECTION

GCN(10). Cyanamide (9.0 g) was added to a porcelain cup and calcined under N_2 flow at 823 K for 4 h with the heating rate being 2.3 K min⁻¹. Grinding of the resultant gave yellow powders of GCN(10).

GCN(x) [x = 56, 160, and 228]. Cyanamide (3.0 g) was mixed with different amount of a Ludox HS40 solution (40% solution of ca. 12 nm silica particles; 3.6, 7.5, and 11.3 g, respectively) and stirred at 333 K for 12 h. The resultant was calcined under N₂ flow at 823 K for 4 h with the heating rate being 2.3 K min⁻¹. The resulting powders were stirred in a NH₄HF₂ solution (4 M) at 298 K for 24 h to remove the silica template particles. The obtained powders were recovered by centrifugation and washed thoroughly with water until the pH of the solution became ca. 7.0. They were then washed with EtOH and dried at 343 K in vacuo for 12 h.

Photoreaction. Each respective catalyst (20 mg) was added to an EtOH/water mixture (9/1 v/v, 5 mL) within a Pyrex glass tube (φ 12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and O₂ was bubbled through the solution for 5 min. The respective tube was immersed in a temperature-controlled water bath $(298 \pm 0.5 \text{ K})^{53}$ and photoirradiated with magnetic stirring using a 2 kW Xe lamp (USHIO Inc.).⁵⁴ A 20 wt % NaNO₂ solution was used as a filter to give light wavelengths at $\lambda > 420$ nm.⁵⁵ The light intensity at 420-500 nm was determined to be 26.9 W m⁻² After the photoreaction, the gas-phase products were analyzed by GC-TCD (Shimadzu, GC-8A). The catalyst was then recovered by centrifugation. The H₂O₂ amount in the resulting solution was determined by a redox titration with KMnO₄. Other liquid-phase products were quantified by GC-FID (Shimadzu, GC-2010).

ESR analysis. The spectra were recorded at the X band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.5

mW, where microwave power saturation of the signals does not occur.⁵⁶ The magnetic field was calibrated with a 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as a standard. The measurements were carried out as follows: catalyst (20 mg) was suspended in an EtOH/water mixture (9/1 v/v, 5 mL) containing DMPO (0.1 mmol) within a Pyrex glass tube (φ 12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. After ultrasonication (3 min) and O₂ bubbling (5 min), the tube was photoirradiated at λ >420 nm with magnetic stirring for 3 min. After the photoirradiation, the catalyst was recovered by centrifugation, and the resulting solution was subjected to ESR analysis.

Electrochemical analysis. The rotating disk electrode analysis was performed on a computer-controlled CHI600D advanced electrochemical system with a three-electrode cell. An Ag/AgCl electrode and a Pt wire electrode were used as the reference and counter electrode, respectively.^{47,49} The working electrode was prepared according to the procedure described in literature:⁴⁹ the respective GCN catalysts (20 mg) were dispersed in water (5 mL) by ultrasonication. The suspension (20 μ L) was put onto a Pt disk electrode and dried at room temperature. Linear sweep voltammograms were obtained in an O₂-saturated 0.1 M phosphate buffer solution (pH 7) with a scan rate being 10 mV s⁻¹ at different rotating speed (400–1600 rpm). After each scan, O₂ was babbled through the electrolyte for 5 min to saturate O₂.

Calculation details. All of the calculations were performed with tight convergence criteria at the DFT level with the Gaussian 03 package, using the B3LYP/6-31G(d) basis set for all atoms. The excitation energies and the oscillator strengths were calculated by TD-DFT at the same level for optimization using the polarizable continuum model (PCM). Cartesian coordinates for the respective single, double, and triple melem-conjugated models are summarized in the end of Supporting Information.

Other analysis. XRD measurements were carried out on a Philips X'Pert-MPD spectrometer. Diffuse reflectance UV–vis spectra were measured on a V-550 UV-vis spectrophotometer (JASCO Corp.) equipped with Integrated Sphere Apparatus (ISV-469) using BaSO₄ as a reference. XPS charts were measured on a JEOL JPS-9000MX spectrometer using Mg K α radiation as the energy source. N₂ adsorption/desorption analysis and CO₂-TPD measurements were carried out on an AUTOSORB-1-C/TCD analyzer (Yuasa Ionics Co., Ltd.). TEM observations were performed using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.⁵⁷

ASSOCIATED CONTENT

Supporting Information

 N_2 adsorption/desorption isotherms (Figure S1); XRD patterns (Figure S2); diffuse reflectance UV-vis spectra (Figure S3); results of photocatalytic decomposition of H_2O_2 (Figure S4); Cartesian coordinates for single, double, and triple melem models. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTOR INFORMATION

Corresponding Author

shiraish@cheng.es.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Grant-in-Aid for Scientific Research (No. 26289296) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT), and by the Precursory Research for Embryonic Science and Technology (PRESTO) from Japan Science and Technology Agency (JST).

REFERENCES

(1) Campos-Martin, J. M.; Blanco-Brieva, G.; Fierro, J. L. G. *Angew. Chem., Int. Ed.* **2006**, 45, 6962–6984.

(2) Shaegh, S. A. M.; Nugyen, N-T.; Ehteshami, S. M. M.; Chan, S. H. *Energy Environ. Sci.* **2012**, *5*, 8225–8228.

(3) Sandelin, F.; Oinas , P.; Salmi, T.; Paloniemi, J.; Haario, H. *Ind. Eng. Chem. Res.* **2006**, *45*, 986–992.

(4) Liu, Q.; Bauer, J. C.; Schaak, R. E.; Lunsford. J. H. Angew. Chem., Int. Ed. 2008, 47, 6221–6224.

(5) Edwards, J. K.; Solsona, B.; Ntainjua, E. N.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. *Science* 2009, 323, 1037–1041.

(6) Teranishi, M.; Naya, S.; Tada, H. J. Am. Chem. Soc. 2010, 132, 7850-7851.

(7) Maurino, V.; Minero, C.; Mariella, G.; and Pelizzetti, E. *Chem. Commun.* **2005**, 2627–2629.

(8) Tsukamoto, D.; Shiro, A.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. *ACS Catal.* **2012**, *2*, 599–603.

(9) Cai, R.; Kubota, Y.; Fujishima, A. J. Catal. 2003, 219, 214-218.

(10) Goto, H.; Hanada, Y.; Ohno, T.; Matsumura, M. J. Catal. **2004**, 225, 223–229.

(11) Hirakawa, T.; Nosaka, Y. J. Phys. Chem. C 2008, 112, 15818–15823.

(12) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.;Carlsson, J. M.; Domen, K.; Antonietti, M. *Nat. Mater.* **2009**, *8*, 76–80.

(13) Thomas, A.; Fischer, A.; Goettmann, F.; Antonietti, M.; Müller, J. O.; Schlögl, R.; Carlsson, J. M. *J. Mater. Chem.* **2008**, *18*, 4893–4908.

(14) Shiraishi, Y.; Kanazawa, S.; Sugano, Y.; Tsukamoto, D.; Sakamoto, H.; Ichikawa, S.; Hirai, T. *ACS Catal.* **2014**, *4*, 774–780.

(15) Shiraishi, Y.; Kanazawa, S.; Kofuji, Y.; Sakamoto, H.; Ichikawa, S.; Tanaka, S.; Hirai, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 13454–13459.

(16) Wang, J.; Ma, J.; Li, X.; Li, Y.; Zhang, G.; Zhang, F.; Fan, X. *Chem. Commun.* **2014**, 50, 14237–14240.

(17) Shiraishi, Y.; Saito, N.; Hirai, T. J. Am. Chem. Soc. 2005, 127, 12820-12822.

(18) Li, L.; Methira, K.; Sebastian W. P.; Morgan S.; Ulrich, W.; Ullrich, S.; Dominik, E. *Chem. Commun.* **2010**, *46*, 7620–7622.

(19) Niu, P.; Zhang, L.; Liu, G.; Cheng, H.-M. *Adv. Funct. Mater.* **2012**, 22, 4763–4770.

(20) Zhang, X.; Xie, X.; Wang, H.; Zhang, J.; Pan, B.; Xie, Y.; *J. Am. Chem. Soc.* **2013**, *135*, 18–21.

(21) Schwinghammer, K.; Mesch, M. B.; Duppel, V.; Ziegler, C.; Senker, J.; Lotsch, B. V.; *J. Am. Chem. Soc.* **2014**, *136*, 1730–1733.

(22) Sano, T.; Tsutsui, S.; Koike, K.; Hirakawa, T.; Teramoto, Y.; Negishi, N.; Takeuchi, K.; *J. Mater. Chem. A* **2013**, *1*, 6489–6496.

(23) Dong, F.; Wanga, Z.; Sun, Y.; Ho W-K.; Zhang, H. J. Colloid Interface Sci. 2013, 401, 70–79.

(24) Martin, D. J.; Qiu, K.; Shevlin, S. A.; Handoko, A. D.; Chen, X.; Guo, Z.; Tang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 9240–9245.

(25) Zhang, G.; Zhang, J.; Zhang, M.; Wang, X. J. Mater. Chem. **2012**, 22, 8083–8091.

Page 9 of 9

ACS	Cata	lysi

- (26) Shi, L.; Liang, L.; Wang, F.; Maa, J.; Sun, J. Catal. Sci. Technol. 2014, 4, 3235-3243. (27) Tahir, M.; Cao, C.; Butt, F. K.; Butt, S.; Idrees, F., Mahmood, N.; Ali, Z.; Aslam, I.; Tanveer, M.; Rizwana, M.; Mahmooda, T. J. Mater. Chem. A 2013, 1, 13949-13955. (28) Gao, J.; Zhou, Y.; Li, Z.; Yan, S.; Wang, N.; Zou, Z. Nanoscale 2012, 4, 3687-3692. (29) Tahir, M.; Cao, C.; Butt, F. K.; Butt, S.; Idrees, F.; Ali, Z.; Aslam, I.; Tanveer, M.; Mahmoodc, A.; Mahmoodc, N.
 - CrystEngComm 2014, 16, 1825-1830. (30) Wang, X.; Maeda, K.; Chen, X.; Takanabe, Kazuhiro, Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. J. Am. Chem. Soc. 2000, 131, 1680-1681.
 - (31) Chen, X.; Jun, Y-S.; Takanabe, K.; Maeda, K.; Domen, K.; Fu, X.; Antonietti, M.; Wang, X. Chem. Mater. 2009, 21, 4003-4005.
 - (32) Su, F.; Mathew, S. C.; Lipner, G.; Fu, X.; Antonietti, M.; Blechert, S.; Wang, X. J. Am. Chem. Soc. 2010, 132, 16299-16301.
 - (33) Maeda, K.; Kuriki, R.; Zhang, M.; Wang, X.; Ishitani, O. J. Mater. Chem. A 2014, 2, 15146-15151.
 - (34) Kiskan, B.; Zhang, J.; Wang, X.; Antonietti, M.; Yagci, Y. ACS Macro Lett. 2012, 1, 546-549.
 - (35) Lee, S. C.; Lintang, H, O.; Yuliati, L. Chem. Asian J. 2012, 7, 2139-2144.
 - (36) Xu, J.; Wu, H-T.; Wang, X.; Xue, B.; Li, Y-X.; Cao, Y. Phys. Chem. Chem. Phys. 2013, 15, 4510-4517.
 - (37) Li, G.; Zhang, D.; Yu, J.-C. Chem. Mater. 2008, 20, 3983-3992.
 - (38) Guo, C.; Holland, G. P. J. Phys. Chem. C 2014, 118, 25792-25801.
 - (39) Ding, Z.; Chen, X.; Antonietti, M.; Wang, X. ChemSusChem 2011, 4, 274-281.
 - (40) Zhu, J.; Xiao, P.; Li, H.; Carabineiro, S. A. C. ACS Appl. Mater. Interfaces 2014, 6, 16449-16465.
 - (41) Harbour, J. R.; Hair, M. L. J. Phys. Chem. 1978, 82,

1397-1399.

- (42) Jiang, H.; Zhu, Y.; Feng, Q.; Su, Y.; Yang, X.; Li, C. Chem. Eur. J. 2014, 20, 3106-3112.
- (43) Guo, Z.; Liu, H.; Jiang, C.; Zhu, Y.; Wan, M.; Dai, L.; Jiang, L. Small 2014, 10, 2087-2095.
- (44) Sheng, H.; Ji, H.; Ma, W.; Chen, C.; Zhao, J. Angew. Chem., Int. Ed. 2013, 52, 9686-9690.

(45) Lin, L.; Zhu, Q.; Xu, A. J. Am. Chem. Soc. 2014, 136, 11027-11033.

(46) Liu, Y. Liu, H.; Wang, C.; Hou, S-X.; Yang, N. Environ. Sci. Technol. 2013, 47, 13889–13895.

(47) Li, S.; Wu, D.; Liang, H.; Wang, J.; Zhuang, X.; Mai, Y.; Su, S.; Feng, X. ChemSusChem 2014, 7, 3002-3006.

- (48) Sun, B.; Ou, Z.; Meng, D.; Fang, Y.; Song, Y.; Zhu, W.; Solntsev, P. V.; Nemykin, V. N.; Kadish, K. M. Inorg. Chem. 2014, 53, 8600-8609.
- (49) Zheng, Y.; Jiao, Y.; Chen, J.; Liu, J.; Liang, J.; Du, A.; Zhang, W.; Zhu, Z,; Smith, S. C.; Jaroniec, M.; Lu, C. Q.; Qiao, S. Z. J. Am.
- Chem. Soc. 2011, 133, 20116-20119.

(50) Sheng, J.; Li, X.; Xu, Y. ACS Catal. 2014, 4, 732-737.

(51) Di, Y.; Wang, X.; Thomas, A.; Antonietti, M. ChemCatChem 2010, 2, 834-838.

- (52) Zhao, L.; Bacsik, Z.; Hedin, N.; Wei, W.; Sun, Y.; Antonietti, M.; Titirici, M.-M. ChemSusChem 2010, 3, 840-845.
- (53) Sugano, Y.; Shiraishi, Y.; Tsukamoto, D.; Ichikawa, S.; Tanaka, S.; Hirai, T. Angew. Chem., Int. Ed. 2013, 52, 5295-5299.

(54) Shiraishi, Y.; Sugano, Y.; Tanaka, S.; Hirai, T. Angew. Chem., Int. Ed. 2010, 49, 1656-1660.

(55) Shiraishi, Y.; Sugano, Y. Ichikawa, S.; Hirai, T. Catal. Sci. Technol., 2012, 2, 400-405

(56) Tsukamoto, D.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. J. Am. Chem. Soc. 2012, 134, 6309-6315.

(57) Shiraishi, Y.; Tanaka, K.; Shirakawa, E.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. Angew. Chem., Int. Ed. 2013, 52, 8304-8308.

