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Highlights

- 5,8-Dicyanopicene film deposited on quartz (CNp/Q) as an organic semiconductor
- CNp/Q enables photocatalytic water decomposition under visible-light irradiation
- CNp/Q enables photocatalytic water decomposition under solar-light irradiation
- 5,8-Dicyanopicene film thickness significantly influences hydrogen-formation rate

Decomposition of water over picene derivatives photocatalyst under visible light irradiation

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Abbreviations

CN-picene: 5,8-dicyanopicene, CNp/Q: CN-picene thin-film on quartz, SEM: scanning electron microscopy, HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital, VB: valence band, CB: conduction band, DFT: density functional theory, DMF: N,N dimethylformamide, SEM: Scanning electron microscope, FT-IR: Fourier-transform infrared spectroscopy, PL: Photoluminescence

Abstract

5,8-dicyanopicene (CN-picene), a picene derivative that absorbs visible-light, was synthesized and its photocatalytic activity for hydrogen production via water decomposition under visible-light irradiation was evaluated. A CN-picene thin-film deposited on a quartz substrate (CNp/Q) was produced by thermal evaporation under vacuum. Hydrogen formation was observed by subjecting CNp/Q to visible-light irradiation in the presence of water. It was confirmed by mass spectrometry using D₂O that the generated hydrogen was derived from water. Water decomposition over CNp/Q photocatalysts with different film thicknesses was also investigated; hydrogen-formation activity increased with film thickness. Furthermore, scanning electron microscopy measurements showed that CN-picene was unevenly deposited on the quartz substrate owing to its aggregation. The surface roughness of the CN-picene film increased with thickness, which consequently increased its surface area; hence, CNp/Q catalysts with thicker films had higher water-decomposition activities than their thinner counterparts.

Keywords: Photocatalytic water decomposition, Organic semiconductor, Hydrogen formation, Picene derivative

Highlights

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1. Introduction

Extensive utilization of fossil fuels in the modern industry has led to energy shortages and greenhouse gas emissions, which are serious global environmental issues. To offset this problem, hydrogen has been proposed as a sustainable and clean energy resource. H_2 production through the photodecomposition of water is regarded as a promising approach because it utilizes sunlight to produce hydrogen gas. It has been developed a large number of photocatalysts since they were first reported by A. Fujishima and K. Honda for the photodecomposition of water under UV light using TiO₂ in 1972 [1-4].

To date, many inorganic semiconductors have been reported as efficient photocatalysts under light or even under solar light [5-7]. In order for a photocatalyst to use sunlight to trigger a chemical reaction, the energy gap of catalyst for the excitation by sunlight had to be controlled and the energy levels of the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) had to be controlled to occur an reduction and oxidation reaction, respectively. However, it is difficult to adjust the energy gap of inorganic semiconductors, which is determined by their unique crystal structures. In contrast, the energy gap of organic semiconductors

can be adjusted, and hence, they are vastly superior to inorganic semiconductors [8,9]. The HOMO–LUMO energy gap of organic semiconductors, which is similar to the valence band (VB) and the conduction band (CB) in inorganic semiconductors, can apparently be easily adjusted by employing intelligent molecular designs such as controlling molecular structures and introduction of substituents. Organic semiconductors have been extensively examined for developing low-cost, flexible and lightweight electronic devices such as photovoltaic cells and light-emitting diodes, et.al. [10]. However, the most organic semiconductors seem to be applied to the electronics field and the studies have hardly ever attempted to use them as photocatalysts.

In our previous work, we used an organic semiconductor, [5]phenacene (i.e., picene), as a photocatalyst for water decomposition under UV-light irradiation [11]. The band gap of picene can be the level required for the water decomposition and corresponds the UV light region. Here, we attempted to extend the light absorption of picene to the visible region because it would allow the maximum use of solar energy. In this work, the HOMO–LUMO gaps of picene derivatives, which can be easily synthesized from picene by introducing substituents, were estimated by density functional theory (DFT) calculations. The calculations indicated that 5,8-dicyanopicene (CN-picene), synthesized by introducing two cyano groups to picene, could absorb visible-light and decompose water.

Hence, we synthesized CN-picene and prepared photocatalysts (CNp(x)/Qs, x = film thickness (nm)) comprising CN-picene thin films deposited on quartz substrates in varying thicknesses by vacuum evaporation. They were then employed in water decomposition to investigate the effect of film thickness on their photocatalytic performances.

2.Experimental

2.1 Chemicals and materials

1-Naphthaldehyde and (1-naphthylmethyl)triphenylphosphonium chloride were purchased from Tokyo Chemical Industry(Tokyo, Japan). Dichloromethane, iodine (I₂), sodium hydroxide (NaOH), bromine (Br₂), sodium thiosulfate (Na₂S₂O₃), sodium hydrogen carbonate (NaHCO₃), copper(I) cyanide (CuCN), *and N,N-dimethylformamide (DMF)* were purchased from Nacalai Tesque (Kyoto, Japan). All reagents were analytically graded and used without further purification. Deionized water and acetone were also used in the experiments.

2.1.1 Synthesis of picene

The synthesis of picene was performed according to the report [12]. 1-Naphthaldehyde (0.156 g) was added in 20 mL of dichloromethane, and added 1 mL of 1.0 M NaOH(aq). Then, (1-naphthylmethyl)triphenylphosphonium chloride (0.438 g) was added and the mixture was stirred at 25 °C for 1 h. Then, water was removed from the mixture by filtration. A solution of I₂ (0.012 g) in 5 mL of dichloromethane was added to the filtrate and stirred overnight using a 500-W Xe lamp (USHIO) under UV irradiation. After filtrating and collecting precipitate, obtained white powder was vacuum dried.

2.1.2 Synthesis of 5,8-dicyanopicene

The synthesis of 5,8-dibromopicene was performed according to the report [13]. Picene (0.094 g), Fe powder (0.011 g), and I₂ (0.012 g) were added to 90 mL of CCl₄. A solution prepared by dissolving Br₂ (0.091 g) in 1.5 mL of CCl₄ was added dropwise to the above solution while mixed at 10 °C for 1 h by magnetic stirrer. The resulting solution was then heated to 25°C and stirred overnight. The solution was further heated to 60 °C and stirred overnight. After cooling to 25 °C, the obtained solution was sequentially washed with concentrated Na₂S₂O₃ (aq.), concentrated NaHCO₃ (aq.), and water. MgSO₄ was added to remove any water and the solution was evaporated to obtain a yellow powder. This powder was recrystallized using toluene to obtain 5,8-dibromopicene. The synthesized 5,8-dibromopicene (0.1 g) and CuCN (0.082 g) were mixed in 10 mL of DMF and refluxed at 120 °C for 24 h under a nitrogen atmosphere. Then, the solution was washed with 28% NH₃ (aq) and water. MgSO₄ was added to remove moisture, and a deep yellow powder was obtained using an evaporator. The product was washed with ethanol to obtain 5,8-dicyanopicene (CN-picene).

2.1.3 Catalyst preparation

After washing a quartz substrate with ethanol and drying it with warm air, a 5,8dicyanopicene film was deposited on its substrate by the vacuum deposition method (SANYU SVC-700TM system). Briefly, the substrate was placed in the vacuum chamber and held at a distance of 25 cm from the molybdenum boat including an organic semiconductor (i.e., CN-picene powder). The pressure inside the vacuum chamber was reduced to 10–2 Pa below, and CN-picene was sublimed by heating the boat at an electric current (~10 A). The CN-picene thin film was then deposited on the quartz (deposition rate of 0.2 nm/s), giving CNp(x)/Q. The film thickness of CNp(x)/Q was estimated from the deposition rate and deposition time.

2.2 Photocatalytic hydrogen production

The water decomposition over organic semiconductor photocatalyst was carried out by a photo-batch-reactor under light irradiation. The prepared photocatalyst and a sacrificial agent (4 ml of 4 M aqueous formic acid solution) were put in a quartz reactor (5.0 mL), then its solution was bubbled by a dry argon gas for 15 min. The entire reactor was replaced with argon gas by these procedures. After the purge, the light was irradiated to the photo-batch-reactor by using a 500-W Xe lamp (USHIO, SX-UI501XQ) through 390 nm cut filter (HOYA UV-39) placing at a distance of 1cm from the lamp window. The photo-reactor was placed at a distance of 5cm from the lamp window. After the light irradiation, the gas phase components in the reactor were analyzed using gas chromatography equipped with a thermal conductivity detector (Shimadzu GC-8A) using Ar carrier. In the repeated tests, the recovered catalyst was washed with 20 ml of water and the reaction using its reused catalyst was carried out in the same procedure as above. Additionally, water photodecomposition over CNp(x)/Q under solar-light irradiation was demonstrated by setting the photo-batch-reactor in a cooling water circulation device and maintaining the reaction temperature at 5 °C.

2.3 Characterization

Scanning electron microscope (SEM) images of the obtained samples were obtained using a JEOL JEM-7500F instrument with an acceleration voltage of 10 kV, an emission current of 20 \Box A and an irradiation current of 8 mA. UV–vis absorption spectra of these prepared samples were measured by Hitachi U-3210D. Fourier transform infrared spectroscopy (FT-IR) spectra were analyzed by Thermo Electron NICOLET380. Pellets for FT-IR measurement were prepared by the KBr method. The photoluminescence (PL) emission spectra were measured by Hitachi F-700.

2.4 DFT calculation

The most stable structures of picene and CN-picene were calculated by using Gaussian 09 software. From those calculation results, the molecular orbitals of the HOMO-LUMO levels were visualized. All calculations were carried out by DFT/B3LYP methods using 6-311G (d, p) basis set.

3. Results and discussion

3.1 DFT calculation of the effect of introducing CN groups on picene

In our previous work, we have shown that picene can function as a photocatalyst under ultraviolet light irradiation (λ > 250 nm) to promote efficient photodecomposition of water [11]. Picene is a p-type organic semiconductor with a HOMO–LUMO energy gap of 3.3 eV. It absorbs visible-light of wavelength 383 nm and excites electrons by $\pi \rightarrow \pi^*$ transition (Fig. 1). The newly synthesized photocatalyst, CN-picene, which has two cyano groups at the 5 and 8 positions (Fig. 2), has a HOMO–LUMO energy gap of 2.7 eV and absorbs visible-light of wavelength 461 nm. Hence, the introduction of two cyano groups into the picene molecule increased the LUMO and HOMO levels by 0.9 and 0.3 eV, respectively. Fig.3 shows the calculated molecular orbitals of the HOMO-LUMO levels of picene and CN-picene. In contrast to picene, the π -electron cloud of the CN-picene molecule extends to its cyano groups and is larger than that of picene. Furthermore, in the CN-picene molecule, the electron cloud of LUMO, including the carbon atoms of 1 and 14b, increases more than that of picene and seems to include the carbon atoms of 4a. As a result, the LUMO level of CN-picene was greatly stabilized, and its electric potential was extremely high.

3.2 Preparation and characterization of CNp/Q

Based on the prediction obtained from the DFT calculation, CN-picene was synthesized, and the synthesized CN-picene was heated in vacuum and deposited on a quartz substrate. FT-IR spectrum of CNp/Q(80) before and after the heating treatment by the vacuum deposition was measured, in order to investigate whether the synthesized CN-picene was not decomposed by this treatment (Fig. S1 and S2). The peak at 2220 cm⁻¹ attributed to CN stretching had the same intensity both before and after vapor deposition (Fig. S2). The other peaks almost showed no change before and after the

deposition (Fig. S1). Therefore, it was shown that CN-picene did not decompose in the process of vapor deposition and was stably deposited on a quartz substrate. The surface of the prepared thin film was observed by SEM (Fig. 4). Compared to the quartz substrate, a large number of aggregates with a short (0.5–1.5 μ m) and a long (1–3 μ m) sides were observed on the surface of CNp(80)/Q. These indicated that a CN-picene thin film formed on the quartz substrate.

Figure 5 and Figure 6 show the UV–Vis spectrum and photoluminescence spectrum of CNp/Q(80), respectively. Quantum chemical calculations showed that CN-picene has absorption peaks at 2.73 eV (λ = 453 nm), 3.16 eV (λ = 392 nm), and 3.37 eV (λ = 367 nm) in order from the long-wavelength side. The actual UV-Vis spectrum measurement of CNp(80)/Q (Fig. 5) confirmed the peaks of approximately $\lambda = 387$ nm and $\lambda = 362$ nm, corresponding to 3.16 and 3.37 eV, respectively. In the simulation performed using DFT calculations, one molecule is virtually present in the vacuum; therefore, the calculation result is on the longer-wavelength side compared to the actual absorption peak[14,15]. Therefore, the calculation result of CN-picene is approximately 5 nm greater than the measured value. In addition, it is considered that these peaks form by the splitting of the LUMO level according to the vibrational state of the molecule and transition from the HOMO level to each vibrational level. As for the absorption at 2.73 eV ($\lambda = 453$ nm), which is considered to be the HOMO–LUMO transition of the CN-picene molecule, a photoluminescence peak was observed at an excitation wavelength of 449 nm (Fig. 6). Similarly, because this transition is, in fact, stabilized by the interaction between molecules, the calculated result is considered to be approximately 5 nm greater than the measured value. The peak at 558 nm in the photoluminescence spectrum is assumed to be the relaxation light from the lowest excited state to the HOMO level. These results suggest successful deposition of CNpicene on the substrate.

3.3 Photocatalytic performance of CNp/Q

The hydrogen-formation rates of water decomposition conducted with and without sacrificial agents under visible-light irradiation over CNp(80)/Q are shown in Table 1. The hydrogen-formation rate was 11.4 μ mol/m²·h when no sacrificial agent was used, confirming that hydrogen was generated by CNp(80)/Q alone. In addition, when a sacrificial agent was added to the reaction, the amount of the generated hydrogen greatly improved. In particular, the highest hydrogen-formation rate (45.6 μ mol/m²·h) was achieved when formic acid was used as the sacrificial agent; this could be because formic acid has a large polarity and is relatively small, and therefore does not sterically hinder the adsorption of water to CN-picene.

A time profile of hydrogen yield via water decomposition with formic acid over CNp(80)/Q under visible-light irradiation was also constructed (Fig. 7). The amount of hydrogen generation increased linearly with the reaction time (0–6 h), and hydrogen generation immediately stopped when light irradiation was cut-off (6–10 h). Hydrogen generation began again at the same formation rate as before when light irradiation was resumed (10–16 h). Fig. 8 shows the recycling tests of CNp(80)/Q, where the hydrogen generation increased linearly with light irradiation for each reuse. The rate of hydrogen

generation was almost constant over three cycles, demonstrating that CNp(80)/Q is relatively stable in the photodecomposition of water under light irradiation.

In order to confirm that hydrogen production was caused by the decomposition of water, mass spectroscopy of the product by a photodecomposition over CNp(80)/Q catalyst using D₂O as a reactant was performed (Fig. S3). As a result, a peak attributable to D₂ was observed at m/z = 4. It was confirmed through mass spectrometry that heavy water (D₂O) was decomposed to generate deuterium (D₂). In addition, m/z = 3 corresponded to HD; HDO was generated by the HD exchange reaction between the H atoms of formic acid or CN-picene and heavy water[16,17]. It was confirmed in Fig. 9 that hydrogen was generated even by solar light irradiation. The hydrogen formation rates during the two runs of reaction were 28.5 and 21.5 μ mol/m²·h, respectively.

3.4 Effect of film thickness on photocatalytic performance of CNp/Q

Figure 10 shows the effect of film thickness of the CNp/Q on the hydrogenformation rate. The hydrogen-formation rate increased when the film thickness is increased up to 200nm. The SEM observation of the film with thicknesses of 80 nm and 300 nm (CNp(80)/Q and CNp(300)/Q, respectively; Fig. 11) showed that the number of CN-picene aggregates of CNp(300)/Q increased in comparison with CNp(80)/Q and these aggregates were stacked perpendicular to the substrate. As the film thickness increases, both the surface area and the hydrogen-generation rate increase. No obvious change was observed in the hydrogen-formation rate between 200 and 300 nm, possibly because the visible-light could not penetrate the film at a certain thickness (200–300 nm). It seemed that the thicker CN-picene thin film had a larger surface area because of the rough surface, hence that the thicker catalyst had a higher activity than the thinner CN-picene thin film.

4. Conclusions

A 5,8-dicyanopicene thin film on the quartz (CNp/Q) was successfully fabricated by vacuum evaporation and used as a photocatalyst in the water photodecomposition under visible-light irradiation to generate hydrogen. It was confirmed by mass spectrometry that water was decomposed to generate hydrogen. The hydrogen-generation activity increases when the film thickness is increased up to 200 nm, after which no obvious change was observed in the hydrogen-formation rate. With the increase in the number of CN-picene aggregates on the substrate, the surface area of the film also increases resulting in a higher hydrogen-generation activity. 5,8-Dicyanopicene was found to be the ideal photocatalyst that can absorb visible-light at approximately λ =461nm. In addition, these HOMO and LUMO levels were 2.16and -1.74eV, respectively, indicating its suitability for the photodecomposition of water. It seems necessary to investigate the effect of substituents on photocatalytic activities, including the reaction mechanism in the future.

CRediT authorship contribution statement

Yuichi Ichihashi: Supervision, Conceptualization, Methodology, Writing-review & editing.
Tomoya Sekiguchi: Investigation, Writing - original draft.
Yuya Tokui: Conceptualization, Methodology, Investigation, Writing - original draft.
Rintaro Hori: Investigation, Writing - original draft.
Shota Naito: Conceptualization, Methodology, Investigation.
Kentaro Okano: Investigation, Synthesis method of 5,8-dicyanopicene.
Atsunori Mori: Methodology, Methodology, Synthesis method of 5,8-dicyanopicene.
Yasuko Koshiba: Investigation, Preparation of organic semiconductor thin film.
Youhei Sutani: Investigation, Preparation of organic semiconductor thin film.
Kenji Ishida: Methodology, Methodology, Writing-review&editing.
Satoru Nishiyama: Conceptualization, Methodology, Writing-review&editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1 Dependence of hydrogen yield on sacrificial agents during water photodecomposition over a photocatalyst comprising a CN-picene thin film deposited on quartz (CNp(x)/Q, x = film thickness (nm)) under visible-light irradiation. Here, x = 80 nm.

Reactant	H ₂ formation rate $[\Box mol/m^2 \cdot h]$
Water	11.4
Water + formic acid	45.6
Water + methanol	27.3
Water + lactic acid	29.3

Figure Captions

Figure 1 Energy gap of picene (a) and CN-picene	; (t))
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- Figure 2 Carbon position number of picene
- **Figure 3** Molecular orbitals of picene (a) and CN-picene (b) (Isovelue = 0.01)
- Figure 4 Scanning electron microscopy (SEM) images of the pristine quartz substrate (a) and CNp(80)/Q (b)
- **Figure 5** UV-vis absorption spectrum of CNp/Q(80)
- Figure 6 Photoluminescence spectrum of CNp/Q(80)
- **Figure 7** Time profile of hydrogen yield in the water decomposition with formic acid over CNp/Q(80) under visible-light irradiation
- Figure 8 Recycling tests demonstrating the reproducible hydrogen yield obtained from water decomposition with formic acid over CNp(80)/Q under visible-light irradiation
- Figure 9 Hydrogen formation from water with formic acid over CNp(80)/Q under solar-light irradiation. RUN1 and RUN2 were carried out under solar-light irradiation in Kobe City, Japan from 12:00 to 14:00 on October 17th and 19th (2018), respectively
- Figure 10 Dependence of film thickness of CN-picene on the quartz on the hydrogen formation rate of water photodecomposition under visible-light irradiation in the presence of formic acid
- Figure 11 SEM images of CNp/Q(80) (a) and CNp/Q(300) (b)
- Figure S1 Full Fourier-transform infrared spectroscopy (FT-IR) spectrum of 5,8dicyanopicene (CN-picene) in a molybdenum boat before (a) and after (b) heat treatment during vapor deposition
- **Figure S2** FT-IR spectrum (2200–2250 cm⁻¹) of CN-picene in a molybdenum boat before (a) and after (b) heat treatment during vapor deposition
- **Figure S3** Mass spectra of products of the photocatalytic decomposition of D₂O with formic acid over CNp(80)/Q



Figure 1



Figure 2







LUMO



Figure 3



(a) Quartz substrate



Figure 5



Figure 6



Figure 7



Figure 8



Figure 9



Figure 10



(b) CNp(80)/Q

(a) CNp(300)/Q

Figure 11



Figure S1



≡



Figure S3