



Application of picene thin-film semiconductor as a photocatalyst for photocatalytic hydrogen formation from water



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ABSTRACT

Interesting photocatalytic properties of a picene thin film on quartz (PTF/Q) have been demonstrated for photocatalytic hydrogen formation from water using several sacrificial agents. Hydrogen is produced in the presence of PTF/Q catalysts under light irradiation, indicating that PTF/Q works as a photocatalyst. The catalyst retains its activity under light irradiation and addition of sacrificial agents enhanced the rate of photocatalytic hydrogen formation from water, similar to the condition when a traditional inorganic photocatalyst is used. Moreover, PTF/Q catalysts comprising picene films of different thickness have been fabricated, and PTF/Q with the thinnest film (50 nm) exhibits the highest activity for hydrogen formation. X-ray diffraction patterns show that the picene crystals are vertically aligned on the surface of the quartz sheet, and that PTF/Q with the thinnest film has a nonuniform film phase. The difference of picene thin-film surface in morphology probably influences the photocatalytic activity. The absorption edge and optical gap energies of the prepared PTF/Q catalyst are determined and the optical gap of the picene film is calculated to be 3.2 eV.

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1. Introduction

Hydrogen has attracted attention as a potential environmentally clean energy fuel, as it can help in overcoming the side effects of greenhouse gas emission and realising a sustainable society [1–3]. In this regard, photocatalytic routes to hydrogen production, in particular the photodecomposition of water, have been the topic of extensive research [4–7]. Many researchers have reported photocatalytic reactions over inorganic semiconductors, with particular focus on enhancing their photocatalytic activity towards the water decomposition reaction. Sacrificial organic electron donors such as alcohols, organic acids, and hydrocarbons often have been employed as hole scavengers to enhance the efficiency of the photodecomposition of water [8–11]. To date, however, most of the photocatalysts used for the aforementioned reaction are inorganic semiconductors with or without sacrificial agents or additives.

Inorganic semiconductors are disadvantageous in that they require a high-temperature annealing step to ensure high performance. It is not easy to induce energy level changes because they have their individual energy levels associated with strong crystal structures. Many studies have investigated inorganic photocatalysts by arbitrarily modifying energy levels. In recent times, organic molecules as photocatalysts are also being increasingly investigated to control the structures and energy levels through band gap engineering approaches such as inorganic-organic hybrids and photo-active MOFs [12]. Here, we show that simple organic semiconductors can function as metal-free organic photocatalysts, which can easily change and control their optical absorption property for extracting hydrogen from water. Organic semiconductors have been used in new applications to replace inorganic semiconductors in various fields of late years. Organic semiconductor crystals have been extensively researched because of their high purity, long-range order, and unique optical structures. Consequently, there has been rapid development in organic electronics based on these crystals (organic light emitting diodes (OLEDs), integrated photonic circuits, and photovoltaic cells), as they have advantageous over traditional silicon-based semiconductor devices [13–18]. Additionally, the

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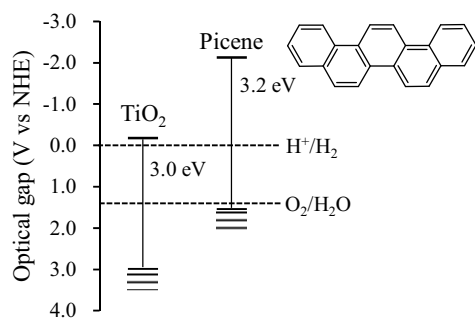


Fig. 1. Energy level diagram of picene and TiO₂.

unique mechanical properties of organic semiconductors allow for the fabrication of flexible electronic devices such as mobile appliances and solar cells, whose market position has been strengthened because of their high mechanical flexibility and ease of mass production [19,20]. However, applications of organic semiconductors have been limited to the field of electronics. The photocatalytic properties of organic semiconductors, which differ from those of traditional inorganic semiconductors in terms of molecular orientation, intermolecular interactions, and wavelength selectivity, have not been investigated in detail, even though organic semiconductors are expected to many unique photocatalytic properties. Consequently, there are only a few reports on the use of organic semiconductors as photocatalysts [21,22]. In this study, we used a photocatalytic system featuring an organic thin-film semiconductor for hydrogen evolution from water. Picene was chosen as the organic semiconductor because its band gap is close to the energy level of typical inorganic semiconductors, such as TiO₂, which is required for the decomposition of water, as shown in Fig. 1 [23,24]. Picene thin-film catalysts were prepared by thermal evaporation under vacuum, and the photocatalytic decomposition of water was performed in the presence of several sacrificial agents to evaluate the photocatalytic performance of the picene catalysts. The reaction was also performed using picene catalysts with different film thickness to investigate the influence of the film-forming state of picene crystal on the photocatalytic performance.

2. Experimental

2.1. Catalyst preparation

Pure picene powder was obtained from NARD Institute, Ltd., Japan. Picene film was deposited on a quartz glass substrate by thermal evaporation under vacuum using a SANYU SVC-700TM system. Before deposition, the substrate (quartz size; 10 mm × 40 mm × 0.5 mm) was cleaned using acetone in an ultrasonic bath, and dried at 333 K. The substrate was then placed in the substrate holder of the deposition system, which was positioned approximately 25 cm above a molybdenum boat containing the picene powder. The holder and boat were placed in a vacuum chamber that was pumped down to a base pressure of 10⁻⁴ Torr by using a diffusion pump. Subsequently, the molybdenum boat was heated by electric current of ~10 A to sublime picene, and the picene film was deposited on the substrate at a deposition rate of 0.2 nm s⁻¹.

2.2. Photocatalytic reaction for hydrogen formation from water

Water decomposition was carried out in a batch reactor system. The prepared catalyst (picene thin film/quartz; PTF/Q) and 5.0 mL aqueous urea solution (0.3 M) were placed in a 7.8 mL cylindrical quartz reactor. Dry argon gas was bubbled through the solution

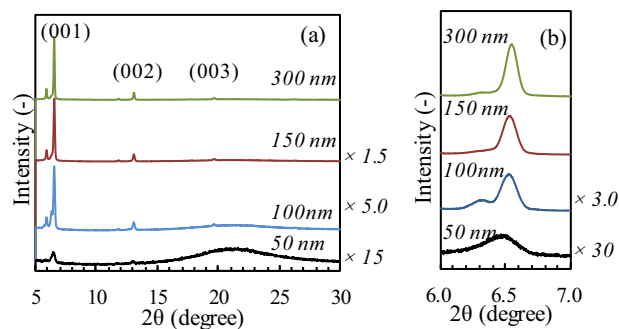


Fig. 2. XRD patterns of PTF/Q of different film thickness; (a) the wide scans in the region 5.0°–30.0°, (b) the narrow scans in the region 6.0°–7.0°.

for 15 min to ensure complete removal of air, and then the entire reactor was purged with argon. The reactor was placed at 5 cm from the window of lamp. Light irradiation was performed by using a 500 W Xe lamp (USHIO, SX-UI501XQ) equipped with a 250 nm cut-off filter (HOYA UV-25) which was positioned at a distance of 1 cm from the window of the lamp. After the reaction was complete, the vapour-phase components were withdrawn by a syringe and analysed by gas chromatography (Shimadzu GC-8A) using a thermal conductivity detector (containing molecular sieve 13x column and Ar carrier).

2.3. Characterisation

The structure and crystallinity of the thin film were characterised by X-ray diffraction (XRD) using a RIGAKU RINT2100 system with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. Standard scans were acquired from 5° to 30° (2θ) at a step size of 0.020° (2θ) and a dwell time of 1 s per step. Fine scans were acquired from 6° to 7° (2θ) at a step size of 0.002° (2θ) and a dwell time of 1 s per step. UV–vis spectra was recorded using a UV–vis absorption spectrophotometer (Hitachi U-3210D) in the region 200–800 nm at a step size of 1 nm. The optical gap was calculated from the absorption edge of the UV–vis absorption spectrum using the formula $\Delta E_{\text{opt}} (\text{eV}) = 1237.5/\lambda$ (in nm).

3. Results and discussion

3.1. Structure of picene thin-film photocatalysts

The structural characterisation of PTF/Q of different film thickness was performed based on X-ray diffraction pattern measured at 298 K. The XRD patterns of the PTF/Q catalysts are shown in Fig. 2. Diffraction lines in Fig. 2(a) ascribable to (001), (002), (003), and (004) reflections are observed, indicating highly oriented single crystal growth of the picene layer with vertical periodicity of 13.5 Å [25–27]. These diffraction patterns give an interphase distance with *c* axis length of 13.5 Å, which corresponds to the slightly tilted phase of picene crystal on a substrate. Picene clusters form a highly ordered and crystalline thin film that is nearly identical to those observed for the *c* axis in single crystals, as shown by the (001) reflections [27]. These reflections indicate that the *a*, *b* planes of the grains are oriented parallel to the substrate surface. Hence, such Bragg reflections are attributed to the vertical orientation of most picene molecules on the quartz substrate [28] (see Fig. S1 in Supporting Information). Fig. 2(b) shows the fine XRD scans in the region 6.0°–7.0°. All diffractions in Fig. 2(b) show two peaks, located at 6.30° and 6.54°, which are assigned to the vertical periodicity of 14.0 Å (Phase 1) and the slightly tilted crystalline phase of 13.5 Å (Phase 2), respectively [29]. The peak profiles were analysed using pseudo Voigt functions (see Fig. S2 in Supporting

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