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## Hydrogen production for photocatalytic decomposition of water with urea as a reducing agent

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### ABSTRACT

Urea is expected to be used as a reducing agent in the photocatalytic formation of hydrogen from water because it is a non-petroleum material and abundant in domestic wastewater. In this study, a TiO<sub>2</sub> catalyst co-doped with tantalum(V) and a trivalent metal cation, serving as promoters, was applied for the photocatalytic decomposition of water for hydrogen production using urea as the reducing agent. Co-doping of TiO<sub>2</sub> with tantalum(V) and a trivalent metal cation resulted in a considerable redshift of the absorption edge of TiO<sub>2</sub> via the formation of impurity levels. In particular, the incorporation of tantalum(V) and chromium(III) into TiO<sub>2</sub> resulted in significant performance enhancement for the photocatalytic decomposition of water for hydrogen production. The products obtained from the photodecomposition of water with urea were also identified, and urea was transformed into N<sub>2</sub> and CO<sub>2</sub> during the reaction. Moreover, the reaction was performed using thin-film photocatalysts based on organic semiconductors, such as picene, representing a class of novel, unconventional photocatalytic materials. Picene thin-films exhibited activity similar to that exhibited by traditional inorganic semiconductors. Effective utilisation of urea has potential application in a green and sustainable production of hydrogen from wastewater via photocatalysis using various semiconductors.

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### 1. Introduction

Currently, the rapidly increasing environmental pollution caused by the dependence on petroleum energy sources is a serious issue worldwide, attributed to the high consumption of petroleum resources and harmful chemicals released into the environment. Thus, for several decades, sustainable chemical processes, as well as environment-friendly energy sources, have been desired in industry [1–9]. In particular, hydrogen has attracted considerable attention as a promising energy carrier for a future low-carbon economy, which is used not only in electrochemical cells, but also as a fuel in internal engines [10–17]. The utilisation of hydrogen as an electrical energy carrier is actually limited because the current production of hydrogen from hydrocarbons requires a large

amount of energy, as well as results in carbon dioxide evolution [18–20]. Therefore, it is imperative to develop green hydrogen production processes for realising a sustainable chemical society, where renewable sources of energy, such as solar energy, can be exploited.

Photocatalytic technology based on semiconductors has attracted considerable attention in the fields of solar energy utilisation and environmental remediation. Several studies have been reported on the development of new semiconductors and their applications in photocatalysis, such as for the photodecomposition and removal of harmful chemical compounds [21–23], photosynthesis of chemical substances [24–26], and photodecomposition of water into hydrogen and oxygen [27,28]. In particular, the production of hydrogen via the photodecomposition of water is an active research area in photocatalysis, which typically utilises reducing agents. However, the use of reducing agents originating from petroleum resources only marginally contributes to savings with respect to the consumption of petroleum resources and emissions of carbon dioxide. Urea is expected to be used as a reducing agent

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for the photocatalytic production of hydrogen as it is a non-toxic organic compound and abundant in domestic wastewater. For photocatalysis, titanium dioxide ( $\text{TiO}_2$ ) is typically used because of its wide range of applications, such as water decomposition, and chemical stability. However, its photocatalytic efficiency is quite low under visible light, which accounts for nearly half of the solar energy incident on the Earth's surface received from the sun [28]. Some researchers have reported the doping of  $\text{TiO}_2$  with various cations for the improvement of photocatalytic efficiency [29–31]. To improve photocatalytic efficiency, it is crucial to control the light absorption property of photocatalysts. This study reported the performance of two photocatalysts: a  $\text{Ta}^{5+}$  and  $\text{Cr}^{3+}$  co-doped  $\text{TiO}_2$  inorganic semiconductor and a metal-free picene organic semiconductor.  $\text{Cr}^{3+}$ -doped  $\text{TiO}_2$  photocatalysts have been reported [32]; however, doping with  $\text{Cr}^{3+}$  often leads to formation of  $\text{Cr}^{6+}$ , leading to decreased photocatalytic efficiency. A high-performance photocatalyst is expected with the addition of a pentavalent metal ion into doped  $\text{TiO}_2$ , caused by charge compensation [33]. In this study, chemically stable tantalum(V) was selected as a doped metal ion. Co-doping with  $\text{Ta}^{5+}$  and  $\text{Cr}^{3+}$  possibly results in the narrowing of the band gap via the formation of new impurity levels between the conduction and valence bands, thereby leading to rapid recombination of electron–hole pairs. A picene thin-film photocatalyst as a noble metal-free photocatalyst was also developed. The utilisation of organic materials is a developing challenge in photocatalysis [34]. A HOMO-LUMO level of them is expected to be easily tuned by molecular design, such as controlling molecular structure and introduction of substituents. Picene, which is one of organic semiconductors, has an optical gap of 3.2 eV. This energy gap is similar to that of typical inorganic semiconductors, e.g.,  $\text{TiO}_2$ , which is required for the decomposition of water. Therefore, it is expected to be an effective photocatalyst for hydrogen production from water. The performance of  $\text{TiO}_2$  co-doped with  $\text{Ta}^{5+}$  and  $\text{Cr}^{3+}$  and picene thin-film photocatalysts was estimated for the photocatalytic decomposition of water with urea. The decomposition product from urea, which has not been clarified thus far, was also investigated. This paper described the possibility of using urea as a non-petroleum reducing agent for the photodecomposition of water over various photocatalysts including  $\text{TiO}_2$ -based inorganic semiconductors and organic semiconductors. The obtained catalysts were characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ultraviolet–visible (UV–vis) spectroscopy.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Preparation of metal-modified $\text{TiO}_2$ photocatalysts

All materials were used as received.  $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$  were commercially obtained from Nacalai Tesque.  $\text{H}_2\text{PtCl}_6$  was purchased from Tanaka Kikinzoku Kogyo. Metal-modified  $\text{TiO}_2$  photocatalysts (M/ $\text{TiO}_2$ , M: dopant, Ni, Cu, Pt, and Ag) were fabricated by impregnation. In a typical process, 1.0 g of  $\text{TiO}_2$  (JRC-TIO-11, Japan Reference Catalyst) and a prescribed amount of metal precursors were completely dispersed in 50 mL of water, followed by evaporation to dryness in a water bath at 363 K. The obtained mixture was dried overnight in vacuum, calcined at 723 K for 5 h in air, followed by reduction under hydrogen for another 3 h. The solid thus obtained was referred to as M/ $\text{TiO}_2$  (M: Ni, Cu, Pt, or Ag).

#### 2.1.2. Preparation of $\text{TiO}_2$ photocatalysts co-doped with Ta and Cr

Doping of  $\text{TiO}_2$  with Ta and Cr was performed by a simple solid reaction method. A specified amount of  $\text{Ta}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  were

added to  $\text{TiO}_2$ , and the mixture was completely mixed. The powder was calcined at 1423 K for 10 h. The solid thus obtained was designated  $\text{Ta}(x)\text{-Cr}(y)\text{-TiO}_2$ , where  $x$  and  $y$  represent the mol% of Ta and Cr dopants, respectively. Modification of  $\text{Ta}(x)\text{-Cr}(y)\text{-TiO}_2$  with Ni was carried out by the method previously described in Section 2.1.1.

#### 2.1.3. Preparation of picene thin-film photocatalysts

Picene can be used as the photocatalyst because its energy level is similar to the redox potential required for the decomposition of water into hydrogen. Picene powder, which was purified by sublimation, was obtained from NARD Institute, Ltd., Japan. A picene thin-film photocatalyst with a film thickness of 300 nm was prepared by thermal vacuum evaporation using a SANYU SVC-700TM vacuum system. Quartz glass used as the film substrate was cut to the predetermined length and thickness (substrate size: 10 mm  $\times$  40 mm  $\times$  0.5 mm). The prepared catalysts were designated as Picene/ $\text{SiO}_2$ .

### 2.2. Catalyst test

A catalyst (20 mg) and 5 mL of an aqueous solution of urea (0.3 mol/L) were added into a quartz-glass batch reactor. The reactor was charged with Ar for completely removing air. The reaction mixture was stirred and irradiated using a 300-W Xe lamp equipped with a colour filter (Hoya UV-25, Japan) for 3 h. The gaseous products were analysed by gas chromatography (Shimadzu GC-8A, Japan) equipped with a thermal conductivity detector (TCD) using Ar as the carrier gas. The products in the reaction were analysed using  $\text{D}_2\text{O}$  instead of  $\text{H}_2\text{O}$  as the reactant with a quadrupole mass spectrometer.

### 2.3. Characterisation

The structures of the  $\text{TiO}_2$  photocatalysts were characterised by XRD with  $\text{CuK}\alpha$  radiation (Rigaku RINT-2100, Japan). Diffuse-reflectance spectra were recorded on a UV–vis diffuse-reflectance (UV–vis-DR) spectrometer (Hitachi U-3210D, Japan), and data were converted from reflectance to absorbance by the Kubelka–Munk method. XPS spectra were recorded at room temperature on an ESCA-3400 (Shimadzu, Japan) electron spectrometer equipped with a Mg  $\text{K}\alpha$  (1253.6 eV) line of the X-ray source. Photoluminescence spectra were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Japan) equipped with a Xe lamp as the excitation light source at 73 K in vacuum. Fluorescence was generated by continuous-wave near-UV excitation at 280 nm.

## 3. Results and discussion

### 3.1. Photocatalytic formation of hydrogen from water with urea over various catalysts

The photocatalytic production of hydrogen was performed over various semiconductor materials via the photodecomposition of water using urea as the non-petroleum-derived reducing agent under light irradiation, and Table 1 shows the results. The photocatalytic activities of Ni/ $\text{TiO}_2$  and Pt/ $\text{TiO}_2$  (Entry 2 and 5) for the formation of hydrogen are superior to those of pure  $\text{TiO}_2$ , Cu/ $\text{TiO}_2$ , and Ag/ $\text{TiO}_2$ . Hence, Ni/ $\text{TiO}_2$  is used as the standard photocatalyst for the decomposition of water with urea as it is more cost-effective than Pt/ $\text{TiO}_2$ . The optimum amount of Ni loading and reduction temperature for catalyst preparation were determined to be 1.0 wt% and 723 K, respectively (Figs. S1, S2, and S3 in the Supporting Information). A low-molecular-weight organic semiconductor, such as picene, exhibits light absorption similar to the band gap of a typical inorganic photocatalyst [34–37]. As shown

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