



Visible-light-sensitive two-step overall water-splitting based on band structure control of titanium dioxide



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ABSTRACT

Visible light-induced two-step overall water splitting was achieved by combining two types of photocatalysts, which were prepared by introducing foreign elements into titanium dioxide (TiO₂) with a controlled electronic band structure. Rutile and anatase TiO₂ were doped with chromium and tantalum to introduce visible-light sensitivity. Under irradiation with only visible light from a 420-nm LED lamp, the simultaneous liberation of hydrogen and oxygen with a molar ratio of ~2:1 was achieved with these two types of TiO₂-based photocatalysts in the presence of iodate ion/iodide ion as a redox mediator.

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1. Introduction

Various photocatalytic materials have been evaluated for water splitting activity because the generated hydrogen (H₂) represents a clean and renewable fuel source [1–4]. Among examined materials, titanium dioxide (TiO₂), with which Fujishima and Honda first demonstrated photoinduced water-splitting [1], is the most promising photocatalyst due to its abundance, nontoxicity, thermal stability and high resistance against photo-corrosion. Despite these advantageous properties, TiO₂ is only sensitive to ultraviolet (UV) light and therefore requires modification for the utilization of visible light. To this end, numerous studies have examined the effects of doping foreign elements into TiO₂ on visible-light induced water-splitting [5–7]. Although doped TiO₂ is able to generate either H₂ or oxygen (O₂) in the presence of sacrificial agents following irradiation with visible light (half reaction of water-splitting), the simultaneous generation of H₂ and O₂ from water in stoichiometric amounts (overall water-splitting) has not been achieved to date.

Several photocatalysts are capable of overall water-splitting under visible-light irradiation when combined with an appropriate cocatalyst and include gallium nitride (GaN)-zinc oxide (ZnO) solid-solution [4,8–10], zinc-germanium oxynitride

((Zn_{1.44}Ge)(N₂O_{0.44})) [11], bismuth-yttrium-tungsten ternary oxide (BiYWO₆) [12], niobium-substituted silver-tantalum oxide (AgTa_{0.7}Nb_{0.3}O₃) [13], and nano-particulate CoO [14]. Combined systems consisting of two specific photocatalysts for H₂ and O₂ production and a suitable redox couple can also function as visible-light sensitive photocatalysts for overall water-splitting (two-step overall water-splitting or Z-scheme overall water-splitting) [15–17]. Recently, our group [18] and Maeda et al. [19] successfully synthesized a combined system consisting of only one mother material, strontium titanate (SrTiO₃)-based and tantalum oxynitride (TaON)-based photocatalysts, respectively. Based on the activities of these systems, it is conceivable that visible-light-sensitive two-step overall water-splitting systems could be constructed by combining only TiO₂-based materials doped with appropriate metal ions. Based on evidence in the literature, chromium (Cr) 3d forms an isolated band in the forbidden band above the valence band (VB) and below the conduction band (CB) of anatase and rutile TiO₂, respectively when Cr³⁺ is doped at a Ti⁴⁺ site [20,21]. Thus, Cr-doped anatase and rutile TiO₂ are expected to function as the H₂- and O₂-production photocatalysts, respectively.

Here, tantalum ion (Ta⁵⁺) was utilized as a counter dopant to Cr³⁺ at Ti⁴⁺ sites of anatase and rutile TiO₂ to maintain charge neutrality. Using this approach to combine Cr- and Ta-codoped TiO₂ photocatalysts in both the anatase and rutile forms, we achieved two-step overall water splitting under visible-light irradiation.

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2. Experimental

2.1. Preparation of TiO₂-based photocatalysts

Cr/Ta-codoped anatase TiO₂ (Cr,Ta-TiO₂(A)) as a H₂-evolution photocatalyst was prepared by a hydrothermal synthesis method using commercial Ti(SO₄)₂ (24.0% purity, 1.92×10^{-2} mol; Kanto Kagaku), CrCl₃·6H₂O (93.0%, 4.00×10^{-4} mol; Kanto Kagaku), and TaCl₅ (4.00×10^{-4} mol; Kanto Kagaku) as starting materials. For the preparation of Cr/Ta-codoped rutile TiO₂ (Cr,Ta-TiO₂(R)) as an O₂-evolution photocatalyst, Ti(SO₄)₂ (1.96×10^{-2} mol), CrCl₃·6H₂O (1.80×10^{-4} mol), and TaCl₅ (1.80×10^{-4} mol) were utilized as the starting materials. The starting materials for the forms of TiO₂ were mixed and stirred in distilled water for 30 min using a magnetic stirrer. The solutions were treated hydrothermally in an autoclave at 140 °C for 12 h, and the resulting mixtures were washed with sufficient distilled water, collected by centrifugation, and dried at 80 °C overnight. The dried mixtures were calcined at 600 °C for 12 h for the anatase form and 900 °C for 24 h for the rutile form, and were then thoroughly ground using a mortar and pestle. As references, non-doped anatase (TiO₂(A)) and rutile (TiO₂(R)) were prepared under identical conditions using only Ti(SO₄)₂.

The deposition of platinum (Pt) co-catalyst onto the synthesized Cr,Ta-TiO₂(A) and Cr,Ta-TiO₂(R) photocatalysts was performed by a photo-deposition method. Briefly, 0.5 g of Cr,Ta-TiO₂(A) or Cr,Ta-TiO₂(R) powder was first dispersed in 100 mL methanol solution (20 vol%) as a hole scavenger. The amount of H₂PtCl₆·6H₂O (98.5% purity; Kanto Kagaku) as the source of Pt needed to give a weight fraction of Pt relative to either Cr,Ta-TiO₂(A) or Cr,Ta-TiO₂(R) of 1×10^{-3} was calculated and then added to the aqueous suspensions of each dispersed photocatalyst. The suspensions were then sufficiently deaerated using liquid nitrogen (N₂). While deaerating the suspensions, a xenon (Xe) lamp (LA-251 Xe; Hayashi Tokei) equipped with an optical filter (Y-44, Hoya) was employed for light irradiation of the suspension for 4 h. The suspension was then centrifuged, washed with distilled water, and the resulting residues were dried at 80 °C overnight. The residues were ground into a fine powder using an agate mortar to obtain the Pt-deposited Cr,Ta-TiO₂(A) (Pt/Cr,Ta-TiO₂(A)) and Cr,Ta-TiO₂(R) (Pt/Cr,Ta-TiO₂(R)) photocatalyst powders. Pt deposition on TiO₂(A) (Pt/TiO₂(A)) and TiO₂(R) (Pt/TiO₂(R)) was also performed by the same procedure, except the Xe lamp was used without an optical filter.

2.2. Characterizations

The crystal structures of the prepared powders were examined by X-ray diffraction (XRD) using a PW-1700 system (Panalytical). UV-vis absorption spectra were obtained by the diffuse reflection method using a V-650 (JASCO) spectrometer. Quantitative analyses were performed by X-ray fluorescence (XRF) using a ZSXFP Primus II system (Rigaku).

2.3. Photocatalytic water-splitting tests

Two types of photocatalytic water-splitting tests were performed in a gas-closed-circulation system, which was filled with argon gas (50 kPa) after deaeration. The amounts of evolved H₂ and O₂ were monitored using an online gas chromatograph (GC-8A; Shimadzu). Each time we performed the water-splitting experiments, a different amount of N₂ was detected. In addition, we repeatedly deaerated this system to a final pressure of 2.5 Pa and then introduced argon gas into the system in the same way. For these reasons, we considered that the detection of N₂ originated from the intruded air from outside, and the effect of residual O₂ (and N₂) in water was possibly excluded [13,18]. Thus, if N₂ was

detected, the O₂ amount was calculated using the following equation: $O_2 = \text{obs. } O_2 - (\text{obs. } N_2 / 0.78) \times 0.21$.

(1) Half reactions of water-splitting: H₂ and O₂ evolution was monitored in the presence of Pt/Cr,Ta-TiO₂(A) or Pt/Cr,Ta-TiO₂(R) (60 mg each) with the aid of iodide ion (I⁻) (sodium iodide (NaI), 99.5% purity, 0.01 mol/L Kanto Kagaku) or iodate ion (IO₃⁻) (sodium iodate (NaIO₃), 99.5% purity, 0.01 mol/L; Kanto Kagaku), respectively, as a sacrificial agent. The examinations were conducted in 10 mL of solution, without adjusting the pH, with constant stirring using a magnetic stirrer and under irradiation with visible light generated from a light-emitting diode (LED) lamp with a wavelength of 420 nm (420-nm LED, LEDH60-420, Hamamatsu Photonics).

(2) Two-step overall water splitting: Photocatalytic overall water-splitting experiments were conducted by adding the sample powders (Pt/Cr,Ta-TiO₂(A): 90 mg, Pt/Cr,Ta-TiO₂(R): 10 mg) to 10 mL I⁻/IO₃⁻ solutions (I⁻: 8 mL, IO₃⁻: 2 mL) as redox mediators. The suspension was constantly stirred using a magnetic stirrer and the pH was not adjusted. The 420-nm LED light was used for light irradiation. As references, the water-splitting experiments were performed under the identical conditions with 90 mg of Cr,Ta-TiO₂(A) in place of Pt/Cr,Ta-TiO₂(A) and 10 mg of Pt/Cr,Ta-TiO₂(R) as well as with 90 mg of Pt/Cr,Ta-TiO₂(A) and 10 mg of Pt/TiO₂(R) in place of Pt/Cr,Ta-TiO₂(R), in addition to 90 mg of Pt/TiO₂(A) and 10 mg of Pt/TiO₂(R).

2.4. Isotope labeled-water splitting

Photocatalytic overall water-splitting tests were also conducted with the Pt/Cr,Ta-TiO₂(A) and Pt/Cr,Ta-TiO₂(R) powders suspended in 10 mL of I⁻/IO₃⁻ solution containing 30% isotopic water (H₂¹⁸O, purity, 97 atom% ¹⁸O; Sigma-Aldrich,) under the same conditions as above. Evolved gas was detected by a gas chromatograph mass spectrometer (GCMS, GCMS-QP 2010 Ultra, Shimadzu) operated in selective-ion mode to monitor for 28 (N₂), 32 (¹⁶O¹⁶O), 34 (¹⁶O¹⁸O), and 36 (¹⁸O¹⁸O) ions. Spectra were measured under the same conditions used for two-step overall water splitting tests. Natural isotopic compositions of ¹⁶O, ¹⁷O, and ¹⁸O are 99.757, 0.038, and 0.205 atm%, respectively [22]. Then, the compositions of ³²O₂ (¹⁶O¹⁶O), ³⁴O₂ (¹⁶O¹⁸O, ¹⁷O¹⁷O), and ³⁶O₂ (¹⁸O¹⁸O) in the atmospheric condition are calculated to be 99.515, 0.409, and 0.000420 atm%, respectively. We plotted the calculated ¹⁶O¹⁸O and ¹⁸O¹⁸O values using the following equation provided that the ¹⁴N¹⁴N was observed as the result of air contamination from outside as mentioned above: $^{16}O^{18}O = \text{obs. } ^{16}O^{18}O - (\text{obs. } N_2 \times 0.21 / 0.78) \times 0.409 \times 10^{-2}$, and $^{18}O^{18}O = \text{obs. } ^{18}O^{18}O - (\text{obs. } N_2 \times 0.21 / 0.78) \times 0.000420 \times 10^{-2}$ (in fact, ¹⁸O¹⁸O was considered to be equal to obs. ¹⁸O¹⁸O due to the extremely small value of 0.000420×10^{-2}).

3. Results and discussion

3.1. Characterization of the prepared photocatalysts

Elemental analyses by XRF indicated that the molar ratios of Ti:Cr:Ta in Pt/Cr,Ta-TiO₂(A) were 0.982:0.004:0.014 and those of Ti:Cr:Ta in Pt/Cr,Ta-TiO₂(R) were 0.992:0.002:0.006. Notably, these molar ratios were not consistent with the starting ratios used in the preparation of the photocatalysts. This discrepancy was attributed to differences in the solubility of Ti, Cr and Ta in aqueous solution under hydrothermal conditions. The analyses also indicated that the molar fractions of Pt relative to Cr,Ta-TiO₂(A) and Cr,Ta-TiO₂(R) were 9×10^{-4} and 5×10^{-4} , respectively. Cr,Ta-TiO₂(A) and Cr,Ta-TiO₂(R) were confirmed to have a single phase of anatase and rutile TiO₂, respectively, in the obtained XRD spectra (Fig. 1a). In addition, the XRD peaks of Cr,Ta-TiO₂(A) and Cr,Ta-TiO₂(R) were shifted

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