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Z-scheme-type conductive-polymer-P3HT/KTa(Zr)O_3 heterojunction composites for enhancing the photocatalytic activity of water splitting

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ABSTRACT

Photocatalytic water splitting on Pt/KTa(Zr)O_3 modified with poly(3-hexylthiophene-2,5-diyl) (P3HT) as a photoconductive organic polymer is investigated. The photocatalyst powder of Pt/P3HT/KTa(Zr)O_3 was synthesized by evaporation to dryness method. The H_2/O_2 production ratio of the unmodified catalyst was 2.90, whereas the H_2/O_2 production ratio become close to 2 (1.66–2.26) with loading P3HT (0.1 wt% to 0.8 wt%). The optimum amount of P3HT added was 0.4 wt% and the H_2/O_2 production ratio was 2.00, which increased the hydrogen production rate by 476 % compared to the unmodified photocatalyst. As a result of the fluorescence lifetime measurement, when the dye and platinum were supported on KTa(Zr)O_3, charge separation into the dye and platinum was confirmed in both UV and visible light irradiation. Irradiation with visible light in addition to UV light increased the water splitting activity, while water decomposition was not performed only with visible light, suggests Z-scheme type water splitting reaction.

1. Introduction

Recently, hydrogen has been receiving attention as an alternative energy to replace fossil fuels. Hydrogen is an abundant element on the Earth, but it does not exist as a free molecule such as oxygen. Therefore, hydrogen is typically generated by the reforming and refinement of hydrogen-containing resources such as the natural gas, coal, and oil [1]. Because these resources generate by-products that cause global warming, the development of a clean hydrogen production process is essential. Water splitting on a photocatalyst is a suitable method. This process generates H_2 and O_2, which are basic elements of water, and a photoproduced electron from the photocatalyst. The process does not generate greenhouse gases. In addition, the system is simpler than that used for the electrolysis of water with a solar cell, which is considered as a clean hydrogen production process. Sunlight is an ideal source of light for water splitting process with the photocatalyst. In sunlight, UV light (~400 nm) accounts for approximately 5% and visible light (400–740 nm) for approximately 50 % [2]. However, photoexcitation on most photocatalysts proceeds by only UV light [3]. Therefore, sunlight, which mostly includes visible light, cannot be effectively used for this process. Therefore, the development of a photocatalyst that responds to visible light is essential. This requirement means the development of a Z-scheme-type photocatalyst, which combines a low band gap semiconductor with a photocatalyst [4]. Water splitting on the Z-scheme-type photocatalyst is a multistage photoexcitation reaction similar to the photosynthesis mechanism used by plants; this approach has been actively studied since water splitting on material containing two types of visible light-responsive photocatalysts has been reported by Abe and Sayama [5–7]. Originally, the charge exchange by the redox medium, such as IO_3^-/I^-, was needed in this process. Oshima et al. developed this system with $HCa_2Nb_3O_{10}$ nanosheets that was sensitized by a Ru-metal complex type of photosensitizer. This system showed a high activity with a high value of 4580 for the turnover number and a long work lifetime, and it had an apparent quantum efficiency of 2.4 % at 420 nm [8]. It has been recently reported that the movement and separation of charge are streamlined by forming a heterocombination between more than two types of semiconductors [9–11]. Wang et al. reported a $BiVO_4$-$SrTiO_3$-based carbon sheet type of photocatalyst that had a solar-to-hydrogen efficiency of over 1.0 % [12,13]. Poly(3-hexylthiophene-2,5-diyl) (P3HT) is one of π-conjugated polymers with the structure shown in Fig. 1, and the material has superior spectrophotometric and electronic properties [14,15]. In recent

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