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Highly selective and efficient photocatalytic reduction of nitrate in water by a tandem reaction system consisting of Pt/TiO_2 and $SnPd/Al_2O_3$: A comparative study of the tandem reaction system with a typical semiconductor photocatalyst, $SnPd/TiO_2$

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ABSTRACT

A tandem reaction system consisting of a photocatalyst (Pt/TiO_2) and a nonphotocatalyst ($SnPd/Al_2O_3$) promoted the reduction of NO_3^- into gaseous products (mainly N_2) under light irradiation ($\lambda > 300$ nm) in the presence of glucose as a hole scavenger. Photocatalytic H_2 evolution ($2H^+ + 2e^- \rightarrow H_2$) proceeded over Pt/TiO_2, and conventional catalytic reduction of NO_3^- with H_2 ($NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^-$) occurred over $SnPd/Al_2O_3$. We optimized the loading amount of Pt on TiO_2, the Sn/Pd ratio, the loading amount of SnPd on Al_2O_3, and the two catalyst dosages. The optimized tandem system gave a high reduction rate of NO_3^- and a high selectivity for gas (94%) from the photocatalytic reduction of NO_3^- in water. On the other hand, a typical semiconductor photocatalyst $SnPd/TiO_2$ with an optimized Sn/Pd ratio and an optimized loading amount of SnPd bimetal on TiO_2 reduced NO_3^- about two-thirds as fast as the tandem system and was less selective for gas (70%). The tandem system suppressed the wasted H_2 formation, resulting in high light use efficiency for the NO_3^- reduction (95%), which is defined as the ratio of the number of electrons consumed for NO_3^- reduction to the total number of electrons consumed for both NO_3^- reduction and photocatalytic H_2 evolution, though the tandem and $SnPd/TiO_2$ systems consumed about the same total number of electrons. The tandem system has two advantages: (i) the Pt/TiO_2 and $SnPd/Al_2O_3$ subsystems can be separately designed to give highly efficient photocatalytic and catalytic reactions, respectively; and (ii) the reaction rates of photocatalytic and catalytic reactions can be easily controlled by changing the catalyst dosage in the reactor. Those advantages brought about a high reduction rate for NO_3^-, high selectivity for gas, and high light use efficiency for NO_3^- reduction in the photocatalytic reduction of NO_3^- in water.

1. Introduction

Photocatalytic reactions over semiconductor photocatalysts, such as TiO_2 and WO_3, proceed sequentially by the following steps: (i) adsorption of substrate onto the surface, (ii) photoabsorption forming photoexcited electrons (e^-) and holes (h^+) in the bulk, (iii) migration of e^- and h^+ to the surface, (iv) participation of e^- and h^+ in reduction and oxidation, respectively, with the substrates on the surface, and (v) recombination of unreacted e^- and h^+. For reactions in aqueous solution, water is included in the substrate in steps (i) and (iv). The observed rates of the chemical reactions, that is, the rates of reactant consumption and product formation, depend on the rates of these steps, unless radical chain reactions occur in solution or gas phase. The rates of steps (i), (ii), (iii), and (iv) positively influence the observed rate, whereas the rate of (v) negatively influences it, if those are involved in the rate-determining step.

Generally, the photocatalytic activity of unmodified (bare) semiconductor photocatalysts is low, but the rate can be dramatically increased by modifying the semiconductor with a small amount of a metal [1–29], which is called a co-catalyst. One function of co-catalysts, such as Pt [1–5] and Pd [6–10], is to prolong the charge-separated state of photoexcited electrons and holes by the trapping of either electrons or holes on the co-catalyst [11]. In this way, the rate of (v) is decreased, although an excess of the co-catalyst increases the rate of recombination of e^- and h^+ [11]. Another function of co-catalysts is to activate substrate

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molecules via adsorption, which accelerates the rate of (iv): for example, NiO_x [12–16] and $Rh_{2-y}Cr_yO_3$ [17–19] for water splitting; Ag [20–22] for CO_2 reduction; and CuPd [23–26] for NO_3^- reduction. For the photocatalytic reduction of CO_2 or NO_3^- in water, the photocatalytic reduction of water (H^+) to form gaseous H_2 can occur in parallel with the target reaction over a co-catalyst with low hydrogen overpotential such as Pt or Pd [23,27,28]. Photocatalytic H_2 evolution lowers the photocatalytic performance for the target reaction, as pointed out by Anderson [27,28] and Lucchetti et al. [30], because photoexcited electrons are wasted to form H_2, rather than reducing the substrates in water. Thus, H_2 production needs to be suppressed to enhance photocatalytic efficiency. Because both reactions (H_2 evolution and the reduction of CO_2 or NO_3^-) proceed on the co-catalyst, the co-catalyst needs to have excellent adsorption of substrate molecules to preferentially promote the reduction of substrates rather than H_2 evolution. If the two functions of the co-catalyst (prolonging the charge-separated state of photoexcited electrons and holes and activating substrate molecules) are maximized simultaneously by optimizing the design of the co-catalyst, including the choice of element, loading amount, crystalline structure, and particle size, then extremely high-performance semiconductor photocatalysts can be obtained. However, it is very difficult, in general, to achieve simultaneous maximization.

To overcome this difficulty, the use of a tandem reaction system has been proposed, in which the photocatalytic/catalytic functions are distributed to separate particles and these are reconstituted in the reaction mixture. Artificial Z-scheme photocatalytic water splitting [31–33], which affords H_2 and O_2, is a great example of function distribution over separate catalysts. In the Z-scheme photocatalytic system, O_2 and H_2 evolution sites are built on separate semiconductor photocatalysts (e.g., WO_3 for O_2 evolution and TaON for H_2 evolution), and the two catalysts are added to the reaction mixture with a redox shuttle between them.

We have previously reported a tandem reaction system consisting of a photocatalyst and a nonphotocatalyst (typical catalyst) for the photocatalytic reduction of NO_3^- in water (Fig. 1a) [34–36]. In the tandem reaction system, H_2 is formed by a photocatalytic reaction over the photocatalyst,

$$2H^+ + 2e^- \rightarrow H_2, \tag{1}$$

and this H_2 reduces NO_3^- in water over the nonphotocatalyst:

$$NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^-. \tag{2}$$

In the tandem reaction system, the photocatalyst and nonphotocatalyst can be developed independently to maximize their performance. In addition, the two reaction rates can be adjusted appropriately by changing the doses of the photocatalyst and nonphotocatalyst in the reaction mixture. Thus, the tandem reaction system has a great potential to become a much better system for photocatalytic NO_3^- reduction in terms of both activity and selectivity than a conventional system of a semiconductor directly combined with a co-catalyst, which we call a single reaction system (Fig. 1b). Based on the concept described above, we have developed a tandem reaction system using a photocatalyst (Pt/TiO_2 [34,35], $Pt/SrTiO_3$:Rh [36]) and a nonphotocatalyst ($SnPd/Al_2O_3$) that shows high photocatalytic activity and excellent selectivity for gases, including N_2 and N_2O.

In the present study, we compared in detail the photocatalytic performance of a tandem reaction system consisting of a Pt/TiO_2 photocatalyst and a $SnPd/Al_2O_3$ nonphotocatalyst with that of a single semiconductor photocatalyst, $SnPd/TiO_2$, to demonstrate the superiority of the tandem reaction system. Before the comparison, the tandem and single reaction systems were comprehensively optimized. In particular, we focused on the reduction rate of NO_3^-, product selectivity, and light use efficiency for NO_3^- reduction. The photocatalytic reduction of NO_3^- in water is a promising method of purifying groundwater polluted with NO_3^-, which is a serious global problem. In the purification of groundwater, the formation of ammonia and ammonium ions is undesirable due to their toxicity, and so the reaction systems should have high selectivity for gaseous products, such as N_2 and N_2O, as well as high photocatalytic activity.

2. Experimental

2.1. Preparation of catalysts

Aeroxide TiO_2 P25 (Evonik) was used as a TiO_2 photocatalyst. Modification of TiO_2 with Pt was conducted by photodeposition. TiO_2 (2 g) was dispersed in distilled water (135 cm^3) and then CH_3OH (15 cm^3, Wako Pure Chemical Industries) and $H_2PtCl_6{\cdot}6H_2O$ (0.04 mol dm^{-3}, Wako Pure Chemical Industries) were added to the suspension. In a Pyrex glass cell, the suspension was sparged with a stream of N_2 (15 cm^3 min^{-1}) for 30 min and then irradiated using a 300 W Xe lamp (Optical Modulex, USHIO) for 3 h with stirring.

The suspension was centrifuged and the supernatant was replaced with distilled water (200 cm^3). The suspension was stirred for a few minutes and centrifuged again. This process was repeated three times. Finally, the catalyst powder was dried in air at 333 K overnight. The obtained catalyst is denoted as Pt/TiO_2.

Supporting Sn and Pd on Al_2O_3 (Aerosil Alu C) was conducted by incipient wetness impregnation. Al_2O_3 was heated in air at 523 K for 4 h before use. An aqueous solution of $PdCl_2$ (0.112 mol dm^{-3}, Wako Pure Chemical Industries) was dropped onto Al_2O_3 (2.0 g), and the resulting wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. An aqueous solution of $SnCl_2{\cdot}2H_2O$ (0.172 mol dm^{-3}, Wako Pure Chemical Industries) was dropped onto the resulting solid, and then the wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. The obtained catalyst is denoted as $SnPd/Al_2O_3$. When we pay

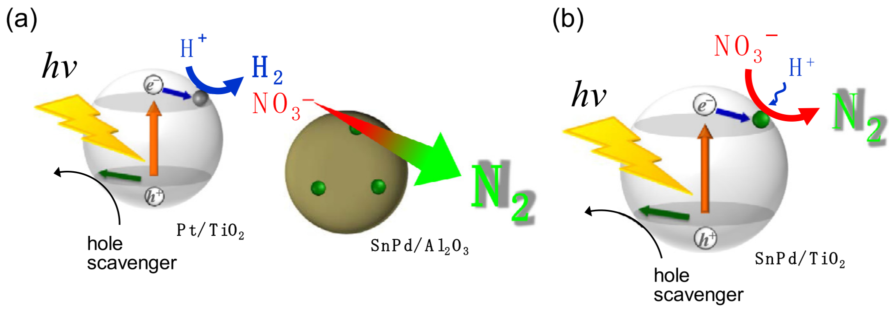

Fig. 1. Schematic images of (a) a tandem reaction system and (b) a single reaction system.