

Green ammonia synthesis from nitrate with photocatalytically generated hydrogen on CuPd nanoalloys supported by TiO₂

Ammonia (NH₃) is not only the main component in chemical fertilizers but also has been noted as an energy carrier for alkaline fuel cells [1]. Presently, we are confronted with both food and energy crises, so a greater demand for NH₃ is therefore forecasted. NH₃, containing no carbon, seems to be far away from contributing to the release of carbon dioxide (CO₂). Since the hydrogen gas produced by fuel reforming is generally utilized for the hydrogenation of inert nitrogen (N₂), industrial NH₃ production is actually accompanied by both a great deal of energy consumption and CO₂ release. The fossil fuel-free H₂ gas produced using renewable energy sources, such as photocatalytically generated H₂ from water utilizing solar light, has therefore received much attention as a clean energy carrier [2], as well as a raw material for various chemical production processes, including that for NH₃. At the same time, over-manuring with synthetic fertilizers increases in the concentrations of the nitrate ion (NO₃⁻) and its derivatives in ground water. Here, we performed the reduction of NO₃⁻ into NH₃ with photocatalytically generated hydrogen as an environmentally benign process that could produce NH₃ without releasing CO₂ and consuming excess energy [3].

Copper-palladium (CuPd) bimetallic alloy nanoparticles loaded on a support are known to be active for NO₃⁻ reduction into N₂ in the presence of hydrogen dissolved in a solution. It has been proposed that the NO₃⁻ ions are firstly reduced to nitrite ions (NO₂⁻) on the bimetallic CuPd surface. Then, NO₂⁻ is reduced to N₂ or NH₃. Previous reports suggested that the distribution of Pd and Cu in the bimetallic particles determines the selectivity in the latter step [4]. On the particulate alloys where Pd atoms form relatively large domains, NO₂⁻ is preferentially reduced into N₂. On the other hand, NH₃ generation appears to preferentially occur on the well-mixed alloy surfaces.

To prepare homogeneously mixed nanoalloys, we synthesized CuPd alloy nanoparticles first. We then deposited them on a TiO₂ support. CuPd nanoalloys were produced by a chemical reduction method using poly[n-vinyl-2-pyrrolidone] (PVP) as a protective reagent to control the alloy size [5].

To investigate the alloy structure in detail, an X-ray diffraction pattern with a high signal to noise ratio was obtained at beamline BL44B2 and is displayed in Fig. 1(a). Although both metals have an fcc structure in the bulk state, the XRD pattern of the nanoalloy was reproduced by assuming a bcc-type structure. This implies that the nanoalloy is constructed from a

homogeneous mixture of Cu and Pd atoms, and not from a mixture of Cu and Pd clusters. Photocatalysts were prepared by the simple mixing of TiO₂ powder (P25) and an aqueous solution of the CuPd nanoalloy. As a reference sample, we also prepared a catalyst with PVP-coated Pd nanoparticles (Pd/TiO₂). The commonly used CuPd bimetallic catalyst (*n*-CuPd/TiO₂) was prepared using the impregnation method. Photocatalytic hydrogen generation and NO₃⁻ reduction under UV irradiation ($\lambda > 300$ nm) were carried out in the presence of methanol as a sacrificial electron donor after the substitution of argon for air in the reaction system. As separate control reactions, we examined NO₃⁻ reduction without UV irradiation, i.e. in the dark, but with *ca.* 350 Torr of added H₂(g), which corresponds to twice the amount of hydrogen generated under UV irradiation for 3 h.

Time courses of hydrogen evolution over CuPd/TiO₂, Pd/TiO₂, and TiO₂ are shown in Fig. 1(b). CuPd/TiO₂ including Cu, on the basis of the amount of a half atomic percentage of the nanoalloy, showed an excellent activity, much higher than that of Pd/TiO₂ [4].

Percentages of residual NO₃⁻, generated NO₂⁻, and NH₃ relative to the initial concentration of NO₃⁻ in the reaction solutions are shown in Fig. 2 [4]. During the reaction over Pd/TiO₂ in the dark, almost none of the products are generated (a). Under UV irradiation, a small amount of NO₃⁻ ions was converted,

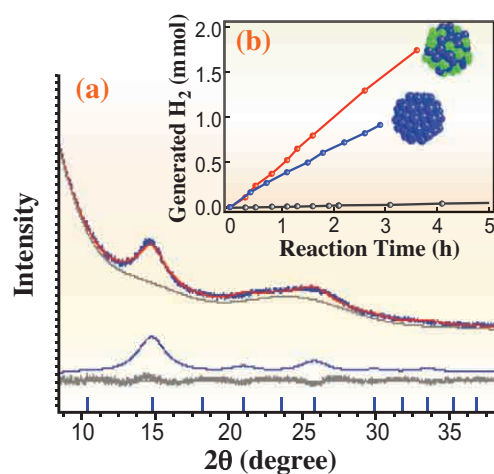


Fig. 1. (a) Powder XRD pattern and Rietveld profile of the CuPd nanoalloy. The observed pattern (blue) was reproduced by the curve calculated assuming a B2-type structure (lattice const. = 3.096(10) Å, diameter = 2.0(6) nm, R_w = 1.57 %, and GOF = 1.56) (red). (b) Time courses of hydrogen evolution over CuPd/TiO₂ (●), Pd/TiO₂ (●), and TiO₂ (●).

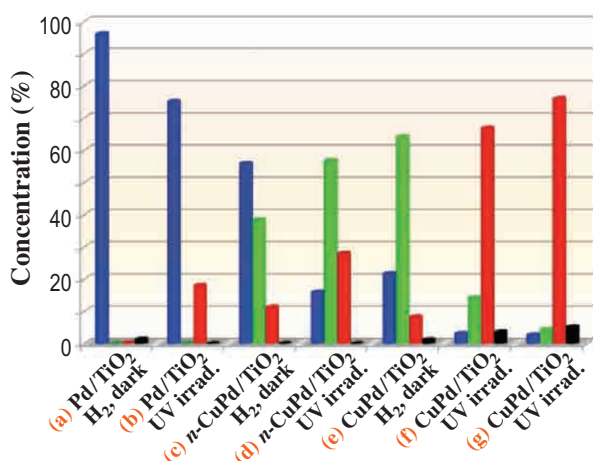


Fig. 2. Concentrations of NO₃⁻ (blue), NO₂⁻ (green), NH₃ (red) and N₂ (black) relative to the initial NO₃⁻ concentration after reaction in a 470 μM NO₃⁻ aqueous solution including 10 vol% methanol. The catalytic reactions were conducted with the following: (a) Pd/TiO₂ (0.46 wt%) with H₂ in the dark and (b) under UV irradiation, (c) n-CuPd/TiO₂ (0.37 wt%) with H₂ in the dark and (d) under UV irradiation, and (e) CuPd/TiO₂ (0.37 wt%) with H₂ in the dark and (f) and (g) under UV irradiation. The reaction time for (a)–(f) was 3 h and that for (g) is 5 h.

15% of them to NH₃ (b). Compared with the results for Pd/TiO₂, a large amount of NO₃⁻ was converted to NO₂⁻ and NH₃ over n-Cu-Pd/TiO₂ in the dark (c). In the reaction over CuPd/TiO₂ in the dark, NO₂⁻ ions were found to be the main product with a concentration of 64% and a small amount of NH₃ was detected (e). On the other hand, a large amount of NH₃ was produced under UV irradiation (f). After 5 h of irradiation, all NO₃⁻ ions were converted and NH₃ was identified as a product with a concentration of 76% (g), which corresponds to 78% of selectivity. This concentration is higher than 28% in the photocatalytic NO₃⁻ reduction over n-Cu-Pd/TiO₂ (d).

To rationalize the high selectivity to NH₃ observed in the reaction over CuPd/TiO₂ under UV irradiation, we propose two explanations. First is the homogeneous mixing of Cu and Pd on the surface of the alloy. NO₂⁻ hydrogenation is considered to be a critical step controlling selectivity towards N₂ and NH₃. As discussed above, we found that Cu and Pd atoms are homogeneously distributed in the CuPd nanoalloy. The percentage of single Pd sites where a Pd atom is directly surrounded by copper atoms is possibly large, resulting in highly selective NH₃ production. Second is the high hydrogenation ability of photocatalytically generated hydrogen. The selectivity of NO₂⁻ hydrogenation over CuPd nanoalloys can be connected to the ratio of the surface coverage of reductant species that of N species (H:N). Given that the amount of hydrogen evolved on CuPd/TiO₂ is

larger than that on Pd/TiO₂, it is likely that hydrogen atoms are generated not only in the proximity of Pd sites but also around Cu sites. It is, hence, supposed that nitrogen oxides absorbed on the surface are continuously surrounded by nascent hydrogen atoms unremittingly. In such a case, a high H:N ratio is attained, resulting in a high selectivity to NH₃. The schematic image is described in Fig. 3.

In the present study, it was found that photocatalytically generated hydrogen exhibits a high selectivity for the conversion of NO₃⁻ to NH₃. Highly selective NH₃ production via NO₃⁻ reduction using hydrogen from solar energy represents a promising approach for fossil-free NH₃ production from waste treatment.

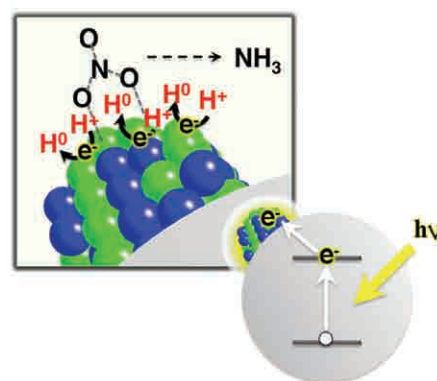


Fig. 3. Schematic image for selective nitrate hydrogenation to ammonia. Adsorbed substrates are surrounded by a large number of nascent hydrogen atoms generated from water.

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