Selective Dinitrogen Conversion to Ammonia Using Water and Visible Light through Plasmon-induced Charge Separation

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Abstract: The generation of ammonia from atmospheric nitrogen and water using sunlight is a preferable approach to obtaining ammonia as an energy carrier and potentially represents a new paradigm for achieving a low-carbon and sustainable-energy society. Herein, we report the selective conversion of dinitrogen into ammonia through plasmon-induced charge separation by using a strontium titanate (SrTiO$_3$) photoelectrode loaded with gold nanoparticles (Au-NPs) and a zirconium/zirconium oxide (Zr/ZrO$_2$) thin film. We observed the simultaneous stoichiometric production of ammonia and oxygen from nitrogen and water under visible-light irradiation.

Ammonia has received much attention as a potential energy carrier and as a fuel for vehicles, in addition to its use as a fertilizer because it is a non-carbon-based chemical that is easily condensed into a liquid. Ammonia is conventionally synthesized through the Haber-Bosch process under high energy consumption conditions. Over 90% of the energy consumed by hydrogen production during ammonia synthesis comes from fossil fuels. Therefore, the development of a new process for synthesizing ammonia without the use of hydrogen gas is needed. The generation of ammonia from atmospheric nitrogen and water using sunlight is one of the preferred approaches to synthesizing ammonia as an energy carrier, and potentially represents a new paradigm for a low-carbon and sustainable-energy society. Although there are several reports about nitrogen photoelectrochemical conversion into ammonia, nitrogen photofixation devices that can harvest visible light exhibit low activity and require a sacrificial electron donor. Herein, we report the selective conversion of dinitrogen into ammonia through plasmon-induced charge separation by using a SrTiO$_3$ photoelectrode loaded with gold nanoparticles (Au-NPs) and a Zr thin film. We observed the simultaneous stoichiometric production of ammonia and oxygen from nitrogen and water under visible-light irradiation.

The co-catalyst is a critical factor in determining the activity and selectivity of a photocatalytic reaction. Ruthenium (Ru) is widely used as a thermochemical and electrochemical catalyst for nitrogen fixation because of its high activity. However, Ru is also known to adsorb H adatoms more strongly than N adatoms, and thereby become poisoned. Therefore, we focused on the binding affinity of H and N adatoms on the surface of a co-catalyst. Density functional theory calculations on a wide variety of transition-metal surfaces have predicted that the adsorption energy of H ($\Delta H^*$) is smaller than that of N ($\Delta N^*$) on the Ru surface. However, $\Delta N^*$ is smaller than $\Delta H^*$ on the Zr surface, indicating that it preferentially adsorbs N adatoms. In fact, our electrochemical experiments indicated that a Zr electrode exhibits greater selectivity for NH$_3$ formation than a Ru electrode (Supporting Information, Figure S1).

Recently, localized surface plasmon resonance (LSMR) of metallic nanostructures has received much attention because of its light-harvesting and electric-field-enhancing effects. These unique properties promote the application of LSMR to many areas, including sensing and photocurrent generation, and photochemical reactions. Previously, we reported a photoelectrochemical reaction using plasmon-induced charge separation on a Nb-doped strontium titanate (Nb-SrTiO$_3$)/Zr photoelectrode fabricated on a 0.05 wt.% Nb-SrTiO$_3$ single-crystalline substrate using an annealing method. A Zr thin film was then deposited using the electron-beam evaporation method onto the opposite side of the Nb-SrTiO$_3$ substrate. The average and standard deviation of the Au-NP size were estimated to be 45 nm and 18 nm, respectively, from a scanning electron microscope image (Figure S2). The surface coverage ratio of the Nb-SrTiO$_3$ substrate by Au-NPs was estimated to be 19.7%. The X-ray photoelectron spectrum (XPS) and X-ray reflection (XRR) revealed that the surface of the Zr film deposited onto the SrTiO$_3$ was oxidized by air, and that the thicknesses of the zirconium oxide (ZrO$_2$) and metal zirconium layers were 2.6 nm and 2.2 nm, respectively (Figures S3, S4). The calculated value of $\Delta N^*$ has been reported to be smaller than that of $\Delta H^*$, even on ZrO$_2$. The scanning transmission electron microscopy images of Au-NPs/Nb-SrTiO$_3$ and Nb-SrTiO$_3$/Zr are shown in Figure 1a. The lattice structure of SrTiO$_3$ and the interface between Nb-SrTiO$_3$ and Zr are observed clearly; however, an obvious periodic structure of Zr was not observed. The cross-section of the Zr layer is considered to be oxidized after sample preparation for the scanning transmission electron microscope measurement. An Au-NPs/Nb-
SrTiO$_3$/Ru photoelectrode was also prepared in a similar manner as the Au-NPs/Nb-SrTiO$_3$/Zr/ZrO$_x$ electrode.

The extinction spectrum of the Au-NPs on the Nb-SrTiO$_3$ substrate is shown in Figure 1b. The spectrum clearly shows that the LSPR band exhibited a maximum at approximately 630 nm. The NH$_3$ synthesis system with an Nb-SrTiO$_3$ substrate loaded with Au-NPs is shown in Figure 1c. The NH$_3$ synthesis device contains two compartments for separate collection of the reduction and oxidation products. To promote NH$_3$ formation, a chemical bias was applied by regulating the pH of these compartments, instead of using an external electrochemical apparatus. The anodic chamber was filled with a potassium hydroxide (KOH) aqueous solution. Simultaneously, an aqueous hydrochloric acid (HCl) solution was injected into the cathodic chamber using N$_2$ gas. The HCl also serves as a proton source for NH$_3$ synthesis.

All of the photoelectrochemical experiments were conducted at room temperature. Figure 2 shows an energy diagram for the plasmon-induced NH$_3$ photosynthesis system with an SrTiO$_3$ photoelectrode loaded with Au-NPs. The principle of this device relies on plasmon-induced charge separation at the Au-NPs/Nb-SrTiO$_3$ interface. We hypothesized that an excited electron is transferred to the SrTiO$_3$ conduction band following the Au-NP interband or intraband transition, or that transfer of an SrTiO$_3$ surface-state electron is induced by the plasmo-induced near-field, or by hot electron transfer. These events result in holes trapped in the SrTiO$_3$ surface near the Au/Nb-SrTiO$_3$/water interface, and these trapped holes can efficiently induce an oxidation reaction. By contrast, the photogenerated electrons injected into the conduction band of SrTiO$_3$, reduced N$_2$ at the Zr/ZrO$_x$ surface, which was deposited on the substrate side opposite of the Au-NPs/Nb-SrTiO$_3$. In this way, plasmon-induced NH$_3$ photosynthesis through nitrogen photofixation was demonstrated.

In the first stage of our work, we investigated the ability of Au-NPs/Nb-SrTiO$_3$/Zr/ZrO$_x$ to form NH$_3$ with ethanol as a sacrificial electron donor. The pH values of the anode and 

![Figure 1.](image1)

![Figure 2.](image2)
cathode solutions were fixed at 13 and 2, respectively. Ethanol (10 vol%) was added to the anodic chamber. The irradiation time dependence of NH₃ formation in the cathodic chamber is shown in Figure 3 a. The Au-NPs were irradiated with light from a xenon lamp, where the light was spectrally filtered to wavelengths from 550 to 800 nm, to excite the LSPR. The amount of NH₃ formed under irradiation of the Nb-SrTiO₃ loaded with Au-NPs linearly increased with increasing irradiation time, and the rate of NH₃ formation was 6.5 nmol h⁻¹ cm⁻². This rate is more than 6-times greater than that in the case where Ru was used as a co-catalyst (1.1 nmol h⁻¹ cm⁻²). Figure 3 b indicates the production selectivity for Zr/ZrO₂ and Ru. In the case of Au-NPs/Nb-SrTiO₃/Ru, the production rate of H₂ was 15-times greater than that of NH₃. This result indicates that proton reduction is the main reaction on the Ru co-catalyst. However, in the case of Au-NPs/Nb-SrTiO₃/Zr/ZrO₂, the concentration of evolved H₂ was smaller than the limit of quantitation (4.7 × 10⁻⁶ mol dm⁻³), and NH₃ was the main product. These results indicate that Zr/ZrO₂ on the Nb-SrTiO₃ exhibits high selectivity and efficiency for NH₃ synthesis. The high reactivity is likely attributable to the adsorbed species on the co-catalyst. Because Zr and ZrO₂ are expected to bind N adatoms more strongly than H adatoms, a large amount of NH₃ is produced compared to the amount of produced H₂. Protons in the solutions are considered to be directly added to an adsorbed N on the Zr/ZrO₂ surface. A mixture gas of N₂ and H₂ (v/v = 1:1) was used instead of pure N₂ gas to confirm the effect of H₂ on the reaction over Au-NPs/Nb-SrTiO₃/Zr/ZrO₂ and Au-NPs/Nb-SrTiO₃/Ru. The formation of NH₃ on Ru on the Nb-SrTiO₃ was significantly enhanced in the presence of H₂ (1.1 to 6.2 nmol h⁻¹ cm⁻²; Figure S5), whereas NH₃ formation on Zr/ZrO₂ on the Nb-SrTiO₃ exhibited similar or slightly lower activity (6.4 to 4.3 nmol h⁻¹ cm⁻²). The positive effect of H₂ to NH₃ synthesis on Ru is considered to be high catalytic ability synthesizing NH₃ from N₂ and H₂ gases. However, the negative effect of the mixture gas of H₂ and N₂ indicate that H₂ is not the main reactant with nitrogen on Zr/ZrO₂. This result supports our hypothesis that the N₂ adsorbed onto Zr/ZrO₂ on the Nb-SrTiO₃ substrate reacts with protons in the solution rather than with H adatoms.

We subsequently attempted plasmon-induced NH₃ synthesis from N₂ and water by using Au-NPs/Nb-SrTiO₃/Zr/ZrO₂ without any sacrificial donor. As a result, the formation of both N₂ and O₂ increased linearly with increasing irradiation time, and the production ratio between N₂ and O₂ was approximately 4:3 (NH₃/O₂ = 1.33; Figure 4 a). The rate of NH₃ and O₂ formation was 0.73 nmol h⁻¹ cm⁻² and 0.53 nmol h⁻¹ cm⁻², respectively. The rate of formation decreased to one-ninth of the rate when ethanol was used as a sacrificial donor. This result indicates that N₂ reduction and water oxidation proceed stoichiometrically. Previously, we reported that water might be efficiently oxidized by multiple stored holes trapped at the surface states of the semiconductor near the hot site of the plasmon. Therefore, both the efficient Zr co-catalyst and the Au-NPs are considered to contribute to the complete redox reaction. The oxidized zirconium nanofilm surface is speculated to also possess excellent catalytic activity for nitrogen fixation because the XPS and XRR results suggest that the metal Zr was covered by the oxidized layer. The bar chart in Figure 4 b shows the action spectrum for the normalized apparent quantum efficiency of NH₃ formation. NAQY₉O₃, NH₃ formation is strongly related to the LSPR excitation because the value of NAQY₉O₃ was highly dependent on the position of the LSPR band (solid line). Additionally, NH₃ formation was observed in all visible wavelength regions, indicating that the plasmon-induced NH₃ synthesis system can efficiently utilize visible light.

We also investigated NH₃ synthesis on Au-NPs/Nb-SrTiO₃/Zr/ZrO₂ from isotopic N₂ gas to obtain direct evidence of N₂ fixation. The photoelectrochemical reaction was promoted by the use of¹⁵N₂ gas (SI Science Co., Ltd.) instead of¹⁴N₂. The formed NH₃ was collected by distillation of the reaction liquid with KOH solution because the cathodic chamber is acidic, and the reaction product was obtained in the form of NH₄Cl. The collected NH₃ was identified by gas chromatography–mass spectrometry (GC-MS). Figure 4 c shows the GC-MS chromatograph of the sample obtained from the reaction solution after 46 h of irradiation time of visible light (wavelength from 550 to 800 nm), and that of a standard NH₃ (2.5 ppm) aqueous solution. A peak derived from¹⁵NH₃ (m/z = 18) was clearly observed at the same
and O synthesis is suitable gas was Plasmon-induced NH formation on the cathodic side of the chamber formation for molecule, as determined using peak intensity from the reaction peak. Reaction rate of NH by using water as an electron donor. a) The irradiation time-

15

14,14

). (green triangle), respectively. The dashed line in black and 18, line in red). The insets show a magnified view from 3.75 to 4.75 min.

Figure 4. Plasmon-induced NH synthesis on Au-NPs/Nb-SrTiO\(_2\)/Zr film by using water as an electron donor. a) The irradiation time-dependence of NH\(_3\) formation on the cathodic side of the chamber (blue diamond), O\(_2\) evolution on the anodic chamber (red square), and ratio of NH\(_3\) and O\(_2\) (green triangle), respectively. The dashed green line indicates the ideal stoichiometric ratio (1.33). The irradiation condition included xenon light spectrally filtered to the wavelengths from 550 to 800 nm. b) Histogram of the action spectrum of the normalized apparent quantum efficiency of NH\(_3\) formation for several wavelength regions. The solid line indicates the LSPR band, which is also shown in Figure 1b. c) GC-MS chromatograph. Upper: sample obtained from the reaction solution after 46 h irradiation time (m/z = 18, line in blue). Lower: 2.5 ppm NH\(_3\) aqueous solution (m/z = 17, line in black and m/z = 18, line in red). The insets show magnified view from 3.75 to 4.75 min.

retention time as a standard \(^{15}\)NH\(_3\) aqueous solution (m/z = 17). Furthermore, the \(^{15}\)NH\(_3\) peak intensity from the reaction solution was much larger than the natural abundance ratio of \(^{15}\)N. Of course, no obvious peak derived from \(^{14}\)NH\(_3\) was observed when \(^{14,14}\)N\(_2\) was used as the reaction gas (Figure S6). These results provide direct evidence that N\(_2\) gas and water were converted into NH\(_3\) under visible-light irradiation.

In conclusion, we report a highly selective and visible-light-responsive plasmonic NH\(_3\) synthesis device containing a Au nanostructure and a Zr/ZrO\(_2\) thin film. N\(_2\) gas was reduced to NH\(_3\) using water as an electron donor under visible light irradiation. Although the energy conversion efficiency of this plasmon-induced NH\(_3\) synthesis is still insufficient for practical use, we expect the efficiency will be improved by increasing the reaction surface area and harvesting the proportion of the incident solar energy flux by fabricating the semiconductors as array structures with large surface areas, such as nanotube or nanohole array structures. Understanding of the plasmon-induced charge separation mechanism and control of electron transport are also important for increasing the efficiency of the plasmonic photoelectrochemical reaction. Our system may help the energy infrastructure and security because sunlight-driven NH\(_3\) synthesis is suitable for use in a distributed energy production system.

Experimental Section

Preparation of Au-NPs and Zr film on an SrTiO\(_3\) substrate: A single crystal of 0.05 wt% Nb-SrTiO\(_3\), (10 × 10 × 0.5 mm\(^3\), Furuchi Chemical) with a (110) surface was used as a semiconductor photodetector for N\(_2\) fixation. Au-NPs were prepared using the reported procedure. A thin Zr film was deposited on the opposite side of the Nb-SrTiO\(_3\) substrate through electron-beam deposition (ED-1500R, SUNVAC) at a deposition rate of 0.05 nm s\(^{-1}\). The morphology of Au-NPs on the Nb-SrTiO\(_3\) was observed using field-emission scanning electron microscopy (FE-SEM, JSM-6700FT, JEOL). The maximum resolution attainable at an electron acceleration voltage of 15 kV was 1 nm. The cross-sectional structures of the Au-NPs/Nb-SrTiO\(_3\) and Zr/Nb-SrTiO\(_3\) interfaces were observed by energy-dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM) performed on a JEOL JEM-ARM 200F operated at 200 kV. The cross-sectional STEM samples were prepared using the focused ion beam technique (JEOL JIB-4600F/HKD) with Ga ions accelerated at a voltage of 30 kV.

Photoelectrochemical reaction: The Au-nanostructured Nb-SrTiO\(_3\) substrate was irradiated in an area of 0.6 mm\(^2\) by a xenon lamp using an arbitrary light intensity and wavelength, and the amount of NH\(_3\) formed per area was calculated by dividing the value by the irradiation area. The apparent quantum yield (AQY, %) of the NH\(_3\) formation system, in which three photons are theoretically required to produce one NH\(_3\) molecule, was determined using Equation (1):

\[
AQY_{\text{NH}_3} = \frac{\text{[Reaction rate of NH}_3\text{ formation (mol s}^{-1}\text{)]}}{\text{[Incident photon flux (mol s}^{-1}\text{)]}} \times 100
\]

The incident photon flux was measured using a spectroradiometer (MSR-7000N, Optoresearch) at each wavelength. The AQY\(_{\text{NH}_3}\) at each wavelength was normalized by dividing the values by the AQY\(_{\text{NH}_3}\) at 550 to 630 nm (AQY\(_{\text{NH}_3}\)). Assays: The quantity of NH\(_3\) formed and evolved O\(_2\) and H\(_2\) were determined using reported methods. The \(^{15}\)NH\(_3\) was quantitatively analyzed using GC-MS. See the Supporting Information for full details of the colorimetric quantity of NH\(_3\) and the gas chromatography conditions.
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