We have successfully developed a plasmon-induced artificial photosynthesis system that uses a gold nanoparticle-loaded oxide semiconductor electrode to produce useful chemical energy as hydrogen and ammonia. The most important feature of this system is that both sides of a strontium titanate single-crystal substrate are used without an electrochemical apparatus. Plasmon-induced water splitting occurred even with a minimum chemical bias of 0.23 V owing to the plasmonic effects based on the efficient oxidation of water and the use of platinum as a co-catalyst for reduction. Photocurrent measurements were performed to determine the electron transfer between the gold nanoparticles and the oxide semiconductor. The efficiency of water oxidation was determined through spectroelectrochemical experiments aimed at elucidating the electron density in the gold nanoparticles. A set-up similar to the water-splitting system was used to synthesize ammonia via nitrogen fixation using ruthenium instead of platinum as a co-catalyst.

1. Introduction

The construction of a light-energy conversion system that uses sunlight for renewable energy with high efficiency is required for the realization of a low-carbon society. Artificial photosynthesis, which stores solar energy as a stable chemical and enables energy use when required, is an important subject [1–4]. The construction of an artificial photosynthesis system that is sensitive to light energy from ultraviolet to near-infrared wavelengths is indispensable for enhancing the solar energy conversion efficiency of artificial photosynthesis. We have studied plasmon-enhanced photocurrent generation using visible and near-infrared light [5,6] as well as plasmon-induced water splitting [7–9]. In this study, we present hydrogen evolution via plasmon-induced water splitting and an artificial photosynthesis system that enables the synthesis of ammonia, which is useful as an energy carrier and for nitrogen fixation. As these types of systems have not been formerly described, it is important to note that, in this study, we developed two similar systems that use visible light irradiation for the evolution of hydrogen and for ammonia synthesis.

Since the discovery of the Honda–Fujishima effect [10,11], research into photocatalysts that use particulate semiconductors has rapidly expanded. Photocatalysts are useful not only for the degradation of organic compounds, but also for hydrogen evolution based on water splitting. Because fuel cells can convert hydrogen to electrical energy with high efficiency, hydrogen serves as an important chemical energy storage material. Family-sized fuel cells were introduced to the market in 2009, and the sale of fuel-cell electric vehicles is scheduled for 2015 in Japan. Although the use of hydrogen has been restricted to industrial applications until now, it is currently being expanded for use as a new energy source. According to an announcement by the Japanese Ministry of Economy, Trade and Industry, energy security has become an important consideration, because the formal introduction of hydrogen power generation is expected to occur in the late 2020s. Specifically, the overseas manufacture of hydrogen, the transportation of hydrogen, hydrogen storage and the construction of hydrogen power generation enterprises are necessary. Moreover, the establishment of a CO₂-free hydrogen feed system that uses renewable energy is expected by approximately 2040 [12].

Ammonia is considered to be an energy carrier owing to its high energy density. In recent years, ammonia has attracted significant attention as a hydrogen carrier and as a new chemical energy source for fuel cells [13–15]. Therefore,
development of a method for efficiently removing hydrogen from ammonia has become an important objective. Specifically, ammonia decomposition technology [16,17], catalytic-cracking catalyst technology [18], ammonia removal technology [19,20] and a pure hydrogen evolution system based on ammonia decomposition [21,22], etc., need to be developed. Moreover, the configuration of a fuel cell system that uses ammonia as a fuel is also an important subject. For this purpose, the construction of a decomposition catalyst, a fuel pole, a cell and its system is required. Furthermore, ammonia can be combusted with a thermomotor for energy transduction or directly combusted to generate heat. In addition, the simple decomposition of ammonia with low energy consumption is also expected. The existing Haber–Bosch synthetic process is a super-high-temperature and high-pressure reaction that may eventually consume large amounts of energy, possibly reaching 1% or more of the total energy used in the world [23]. Therefore, it is necessary to develop an alternative process with a small environmental impact. To help achieve a hydrogen-based society, Japan is furthering the research and development of ammonia as an energy source with a greater energy density than hydrogen. Although this objective is still in the stage of fundamental research, it is now one of the priorities of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Artificial photosynthesis has attracted attention as a method for storing useful chemical energy, such as hydrogen and ammonia, without any environmental impact. Because the required components for hydrogen and ammonia generation are water, nitrogen and sunlight, these energy storage products can be generated using reactants that are virtually infinitely available on the Earth. Although artificial photosynthesis has been just a dream until now, this technology must be realized in Japan because it does not depend on nuclear power generation and represents a source of renewable energy. Prof. Dr Haruo Inoue at Tokyo Metropolitan University is leading the KAKENHI project (grant-in-aid for Scientific Research on Innovative Areas by MEXT) on artificial photosynthesis in Japan (43 research groups participate in this project). This research is based on the fusion of fields, including organic and inorganic chemistry, materials science and so forth, and is aimed at new possibilities for effective artificial photosynthesis. Industrial applications are expected to be possible if the sunlight energy conversion efficiency of hydrogen evolution using artificial photosynthesis reaches 5–10%; therefore, the present target of basic scientific research is achieving 5% conversion efficiency [24,25]. For this purpose, it is important to effectively use visible and near-infrared light and to achieve efficient charge separation. The plasmon-induced charge separation between gold nanoparticles and oxide semiconductor interfaces studied here can act as a co-catalyst in water oxidation, which is considered to be a bottleneck process in water splitting. Thus, this system is promising for artificial photosynthesis and is expected to be deployed in the future.

### 2. The surface-plasmon-induced water-splitting system

We recently constructed a surface-plasmon-induced water-splitting system using a gold-nanostructured oxide semiconductor photoelectrode [26]. In recent years, studies related to solar cells and to the elucidation of relevant mechanisms using photoelectrochemical measurements have been performed using gold-nanoparticle-loaded titanium dioxide photoelectrodes [27,28]. We have also demonstrated the use of gold-nanostructured titanium dioxide single-crystal photoelectrodes (0.05 wt% Nb-doped titanium dioxide (110); Furuuchi Chemical Co.) to achieve efficient photoelectric conversion from visible to near-infrared wavelengths [2,3]. The unique feature of this system is that water serves as an electron source for the photocurrent generation. Thus, the Honda–Fujishima effect might also be observed during visible and near-infrared light irradiation. Four water oxidation reactions proceeded very efficiently on the gold-nanoparticle-loaded titanium dioxide electrode surface. Plasmon-induced charge separation behaves like a co-catalyst for oxygen evolution. During water splitting, the electrochemical potential of hydrogen evolution is also important. Therefore, in this study, a strontium titanate (SrTiO3) single-crystal substrate, which has a conduction-band electrochemical potential that is 0.2 V more negative than that of titanium dioxide (TiO2), was employed.

On the front surface of a Nb–SrTiO3 single-crystal substrate (0.05 wt% Nb-doped SrTiO3 (110); Furuuchi Chemical Co.), gold nanoislands (Au-NIs) were prepared using an annealing method after a gold thin film was deposited. The Nb–SrTiO3 substrate was sequentially cleaned in an ultrasonicator for 5 min using acetone, methanol and pure water. After the organic matter stuck to the surface was removed by irradiation with an excimer lamp for 5 min under an oxygen environment, a 3-mm-thick layer of gold was deposited onto the substrate using a Helicon sputtering machine (MPS-4000, ULVAC). Au-NIs were formed on the substrate by heating at 800°C under a nitrogen atmosphere for 1 h. The platinum plate (Pt, 10 × 10 × 0.3 mm3; Nilaco Co.), which is the hydrogen-evolution co-catalyst, was pasted onto the back of the Au-NI-loaded Nb–SrTiO3 substrate using indium–gallium alloy to provide an ohmic contact. A scanning electron microscope image of the Au-NIs prepared on the Nb–SrTiO3 substrate surface is shown in figure 1a. We confirmed that the average size of the structure is 52 nm with an estimated variation of 10 nm. When the localized surface plasmon resonance spectrum of the fabricated structure was measured, the plasmon resonance band had a peak at 610 nm.

The fabricated Au-NIs/Nb–SrTiO3/Pt electrode was installed in the reaction cell as shown in figure 1b. The front of the substrate (the Au-NIs) served as the anode, and the back of the substrate (the platinum side) served as the cathode for the reaction. The balance of charge between the two electrolysis chambers was maintained using a salt bridge. The chemical bias was controlled by regulating the pH of the two electrolysis chambers. The expected mechanism is explained as follows: the plasmon resonance is first induced by visible and near-infrared light, and the enhanced optical near-field excites an electron from the gold nanoparticles or from the surface-state electron of the Nb–SrTiO3. The excited electron is transferred to the conduction band of the Nb–SrTiO3. The electron that arrived at the back of the substrate reduces a proton on the Pt surface and hydrogen is evolved from the cathode. Conversely, the hole left behind on the Au-NIs oxidizes water or OH−, and oxygen is evolved from the anode. The water oxidation appears to proceed efficiently, because the hole does not remain in the Au-NIs. Moreover, multiple holes are trapped in the surface states of Nb–SrTiO3 in a spatially selective nanoparticle near the Au-NIs/Nb–SrTiO3/water interface, thus allowing for oxidation of the
Therefore, it can be concluded that the plasmon-induced charge separation behaves like a co-catalyst for oxygen evolution. We reasoned that the generated holes did not remain in the Au-NIs, because the Fermi levels ($E_F$) of Nb–SrTiO$_3$ and Au coincide when the Au-NI contacts the surface of Nb–SrTiO$_3$. It is known that $E_F$ exists slightly below the conduction band energy of Nb–SrTiO$_3$. Because the generated holes might easily migrate to the $E_F$, the holes will lose the capability of oxidizing water in a thermodynamically favoured manner, because the potential difference between the flat band potential and $E_F$ is approximately 0.9 V when Au is in contact with TiO$_2$ [29]. The main characteristic of the water-splitting system is that hydrogen and oxygen are produced separately and can be removed from the different electrolysis chambers. Additionally, only the Au-NI side needs to be irradiated, which reduces the area required for light irradiation, because the reduction of the proton is a dark reaction.

The Au-NIs were irradiated using a xenon light with an emission maximum at 600 nm (spectrum width 100 nm, 0.7 W cm$^{-2}$) and plasmon-induced water splitting was attempted. Gas chromatography–mass spectrometry (GC–MS 2010-plus; Shimadzu) was used to quantify the amount of oxygen gas produced. Therefore, water containing $^{18}$O isotopes was used in the electrolysis chamber (anode side), and the amount of $^{34}$O$_2$ was determined using GC–MS. A typical GC–MS chromatogram of the sample after the anode-side chamber of the water-splitting device was irradiated with visible light for 5 h is shown in figure 2a. The pH was 1 on the cathode side and 13 on the anode side. The mass-to-charge ratios ($m/z$) of $^{32}$, $^{34}$, $^{36}$ and $^{40}$ corresponded to $^{32}$O$_2$, $^{34}$O$_2$, $^{36}$O$_2$ and $^{40}$Ar gas chromatograms, respectively. The area of the gas chromatogram was used to calculate the gas concentration. The $^{36}$O$_2$ peak overlapped with the peak of $^{36}$Ar, an isotope in the reference gas used for quantitative determination. Because it was difficult to distinguish these peaks from each other, $^{36}$O$_2$ was not used to determine the amount of evolved O$_2$ gas. To prevent contamination from the air during the measurement, $^{35}$O$_2$ was also excluded from the determination. Thus, the $^{34}$O$_2$ gas chromatogram was used to quantitatively determine the oxygen evolution, which was then compared with the natural abundance ratio. The calibration curve of $^{34}$O$_2$ using $^{40}$Ar as a reference gas is shown in figure 2b. The grey-coloured region corresponds to the data range obtained through the experiments described in this study. The quantity of oxygen gas produced.
of hydrogen gas produced was determined using general gas chromatography.

Figure 3a shows the measured quantities of the evolved hydrogen and oxygen as a function of the light irradiation time. When the pH of the anode side was 13 and the pH of the cathode side was 1 (i.e. the chemical bias was equivalent to 710 mV), the amounts of evolved hydrogen and oxygen increased linearly with increasing irradiation time. A similar response was clearly observed when the pH of the anode side was 11 and the pH of the cathode side was 1 (i.e. the chemical bias was equivalent to 590 mV), although the evolution efficiency decreased compared with the pH combination of 1 and 13. Notably, the difference in the water-splitting efficiency at different pH values on the cathode side was thought to be caused by the difference in the chemical bias between the anode and cathode chambers. In addition, because the amounts of evolved gases remained linear with the irradiation time, this water-splitting system operated stably even after 48 h. We determined that the water splitting proceeded stoichiometrically, because the quantity of evolved hydrogen was twice that of the evolved oxygen. As a control experiment, an analogous experiment was performed without Au-NIs or the Pt co-catalyst with a pH combination of 1 and 13. No hydrogen or oxygen was detected in the case without Au-NIs, whereas the water-splitting efficiency was low without the Pt co-catalyst. We subsequently measured the action spectrum of the evolved hydrogen. As shown in figure 3b, the action spectrum of the evolved hydrogen was consistent with the form of a plasmon resonance spectrum and exhibited good coincidence. Therefore, we confirmed that plasmon-induced water splitting occurred in the system and that hydrogen and oxygen gases were evolved from both surfaces of the Nb–SrTiO₃ substrate.

As shown in figure 3a, the evolution efficiencies of hydrogen and oxygen clearly changed with the pH of the solutions. Therefore, we carefully explored the pH dependence. When the pH at the cathode was fixed to 1 and the pH at the anode was increased from 6.8 to 10, hydrogen was evolved owing to the reduction of protons at the cathode, whereas oxygen was evolved owing to the oxidation of water molecules via a four-electron reaction. Therefore, the water-splitting reaction did not exhibit a significant pH dependence.

When the pH at the anode was increased from 11 to 13.5, oxygen was evolved owing to the oxidation of water molecules and OH⁻ ions. The amount of evolved gases increased gradually as the pH was increased at the anode. Similarly, when the pH at the anode was fixed at 13 and the pH at the cathode was gradually increased from 1, the quantity of the evolved gases decreased, because the proton concentration at the cathode decreased with increasing pH. Neither gas was detectable at pH 4 on the cathode side. On the basis of these results, we hypothesized that hydrogen evolution was the rate-limiting process of the water-splitting reaction. Because water splitting did not proceed when the pH at the anode was 6, the minimum chemical bias in this system was estimated to be 230 mV, which corresponds to the combination of pH 3 (cathode side) and pH 6.8 (anode side). Although water oxidation is the rate-limiting process in a typical water-splitting system, we concluded that the water splitting proceeded at a relatively low chemical bias of 230 mV, because the plasmon-induced charge separation efficiently oxidized the water.

### 3. Surface-plasmon-induced charge separation as determined by spectroelectrochemistry

We performed photocurrent measurements to determine the electron transfer between Au-NIs and titanium dioxide. The efficient water oxidation was determined from the spectroelectrochemical study used to elucidate the electron density in the Au-NIs. As described before, plasmon-enhanced photocurrent generation was clearly observed using a gold-nanoparticle-loaded photoelectrode irradiated by visible and near-infrared light in aqueous electrolyte solution. O₂ evolution occurred as a result of water oxidation, which was a half reaction of water splitting. The photocurrent generation and water oxidation were considered to be due to the plasmon-induced charge separation between Au-NIs and Nb–TiO₂ following the electron transfer reaction. If the generated holes remained in the Au-NIs after electron transfer from Au-NIs to Nb–TiO₂, the electron density in the Au-NIs changed. The surface plasmon resonance is the collective electron movement near the metal surface. Thus, the electron density in Au-NIs was considered to affect the peak wavelength of

**Figure 3.** (a) The irradiation time dependence of H₂ and O₂ evolutions in the cathode and anode chambers, respectively. Closed and open symbols indicate H₂ and O₂ evolution, respectively. (Red, pH combination of 1 and 13; blue, pH combination of 1 and 11; green, without platinum; black, without Au-NIs.) (b) The action spectrum of H₂ evolution is depicted as a histogram of H₂ evolution over several wavelength regions.
the plasmon resonance spectrum. The localized surface plasmon resonance wavelength ($\lambda$) is defined according to the following equation [30,31]:

$$\lambda = \lambda_p \sqrt{\varepsilon_\infty + \left( \frac{1 - L}{L} \right) \varepsilon_m}$$

(3.1)

and

$$\lambda_p = \frac{2 \pi c}{\omega_p} = \sqrt{\frac{4 \pi^2 e^2 m_{\text{eff}}}{N e^2}},$$

(3.2)

where $\omega_p$ is the bulk plasma frequency, $\varepsilon_\infty$ is the permittivity of the high-frequency contribution, $L$ is the particle size shape parameter, $\varepsilon_m$ is the permittivity of the surrounding media, $N$ is the electron density, $e$ is the charge of the electron, $m$ is the effective mass of the electron and $\varepsilon_0$ is the permittivity of free space. Therefore, the electron density in the metallic nanoparticles played a key role in the peak wavelength of the plasmon resonance spectrum. It is known that the plasmon resonance spectrum shows a wavelength shift when the electron density in metallic nanoparticles changes. The plasmon resonance spectrum shows a redshift when electron density $N$ in the metallic nanoparticles decreases. By contrast, a blueshift occurs when the electron density increases, because the change in the Fermi level affects the bulk plasma frequency.

To explore the plasmon-induced charge separation, we performed in situ spectroelectrochemical measurements during the plasmon-enhanced photocurrent generations by monitoring the spectrum shift of the plasmon resonance spectrum. Figure 4a depicts a schematic of the spectroelectrochemical measurement system under photocurrent generations. The Au-NIs/Nb–TiO$_2$ photoelectrode was confined to a small electrochemical cell containing an aqueous potassium chloride (0.1 mol dm$^{-3}$) electrolyte solution. The Pt wires acted as the counter (CE) and quasi-reference electrode. To determine the electron transfer between Au-NIs and Nb–TiO$_2$, the Fermi level of the semiconductor was first controlled by applying an external potential. When a negative potential was applied to the Au-NIs/Nb–TiO$_2$ working electrode (WE), the Fermi level shifted negative as a result of electron transfer from the Nb–TiO$_2$ to Au-NIs.

Figure 4b shows the extinction spectra of Au-NIs with different applied potentials. The spectrum shift of the plasmon resonance band was clearly observed when the applied potential was changed from 0 to $-2.0$ V versus Pt. The onset potential of the spectrum shift was around $-0.5$ V versus Pt, which corresponded to the flat band potential of the Nb–TiO$_2$. The almost linear relationship between the peak wavelength of the plasmon resonance spectrum and the applied potential was clearly seen, as shown in figure 4c. These data indicate that the electron transfer proceeded from Nb–TiO$_2$ to Au-NIs,
and electrons accumulated in the Au-NIs when the negative potential was applied to the Au-NIs/Nb–TiO₂ WE.

Using the same Au-NIs/Nb–TiO₂ photoelectrode, we measured the plasmon resonance spectra of Au-NIs by applying positive potentials under the irradiation of visible light (λ = 450 nm, halogen light). The incident light was also used as a probe light for the spectrum measurement. Although the number of the electrons transferred from the plasmon-excited Au-NIs to Nb–TiO₂, which was estimated from the photocurrent measurement (figure 5a), was sufficient for the detection of spectrum shift, the plasmon band of Au-NIs did not show any spectrum shift even when the Au-NIs/Nb–TiO₂ photoelectrode was irradiated with intense light (1.0 W cm⁻²), as shown in figure 5b. Because no spectrum shift was observed when an acetonitrile solution was employed, it is possible that the plasmonically enhanced optical near-field might have promoted the excitation of the surface-state electrons of the Nb–TiO₂, and, subsequently, the generated hole could have been trapped in the surface state. Therefore, we concluded that the plasmon-induced charge separation behaved like a co-catalyst for oxygen evolution and promoted efficient water oxidation.

Figure 5. (a) Photocurrent responding to turning the visible light on and off at lower (black, 20 mW cm⁻²) and higher (red, 1.0 W cm⁻²) intensities. The applied potential was set at +0.3 V versus Pt. (b) Plasmon resonance spectrum under the irradiation of visible light with lower (black, 20 mW cm⁻²) and higher (red, 1.0 W cm⁻²) intensities.

Figure 6. (a) A schematic of the NH₃ synthesis device with a Nb–SrTiO₃ photoelectrode loaded with Au-NIs. (b) A scanning electron microscope image of Ru on Nb–SrTiO₃ prepared using electron-beam evaporation.

Figure 7. The dependence of NH₃ formation at the cathode side of the chamber on the irradiation time. Nb–SrTiO₃, with irradiation (red square); Nb–SrTiO₃ loaded with Au-NIs and Ru without irradiation (black circle); and Nb–SrTiO₃ loaded with Au-NIs and Ru with irradiation (blue diamond). Irradiation was performed using xenon light that was spectrally filtered to include wavelengths from 550 to 800 nm.
4. Surface-plasmon-induced ammonia synthesis system

Based on the analogous method of the plasmon-induced water-splitting system, we have successfully constructed an artificial photosynthesis system that synthesizes ammonia via a six-electron reduction reaction of a nitrogen molecule under visible-light irradiation [32]. In contrast to the water-splitting method, ruthenium instead of platinum was used as a co-catalyst for the ammonia synthesis, and a gas was used instead of a solution system to reduce the nitrogen gas at the cathode. Therefore, a salt bridge was not used in this system. Au-NIs were prepared on the front surface of a Nb–SrTiO₃ substrate, and a ruthenium film with a thickness of 3 nm was deposited as a co-catalyst via electron beam physical vapour deposition (ED-1500R; SUNVAC Co.) such that Au-NIs/Nb–SrTiO₃/Ru was formed.

The fabricated Au-NIs/Nb–SrTiO₃/Ru electrode was installed in the reaction cell, as shown in figure 6a. The front of the substrate, i.e., the Au-NIs side, served as the anode, whereas the back of the substrate, i.e. the Ru side, served as the cathode. The reaction chamber on the anode side was filled with a 0.1 mol dm⁻³ solution of sodium hydroxide aqueous solution, whereas the back of the substrate, i.e. the Ru side, served as the cathode. The reaction chamber on the anode side was filled with ethanol (EtOH: 10 vol%) as a sacrificial electron donor for oxidation. The reaction chamber on the cathode side was filled with a 0.1 mol dm⁻³ solution of 3 sodium hydroxide aqueous solution, where the back of the substrate, i.e., the Ru side, served as the cathode. Therefore, a salt bridge was not used in this system. Au-NIs were prepared on the front surface of a Nb–SrTiO₃ substrate, and a ruthenium film with a thickness of 3 nm was deposited as a co-catalyst via electron beam physical vapour deposition (ED-1500R; SUNVAC Co.) such that Au-NIs/Nb–SrTiO₃/Ru was formed.

The fabricated Au-NIs/Nb–SrTiO₃/Ru electrode was irradiated using a xenon lamp spectrally. The Au-NIs were irradiated using a xenon lamp spectrally filtered to include wavelengths from 550 to 800 nm, and the amount of ammonia evolved was quantitatively determined. As shown in figure 7, the quantity of the ammonia evolved increased linearly with increasing time of light irradiation at an evolution rate of 0.231 nmol h⁻¹. Ammonia evolution was not observed when Nb–SrTiO₃ without Au-NIs was irradiated or when the Au-NIs/Nb–SrTiO₃/Ru electrode was not irradiated, as shown in figure 4.

As shown in figure 8, the action spectrum of the apparent quantum efficiency of ammonia evolution at each irradiation wavelength matched the plasmon resonance spectrum of the Au-NIs. Furthermore, as shown in figure 8b, even when the plasmon resonance wavelength was altered by decreasing the diameters of the Au-NI particles, the action spectrum of the quantum efficiency still matched the plasmon resonance spectrum. Therefore, we succeeded in the photoelectrochemical synthesis of ammonia using visible-light irradiation and plasmon-induced charge separation.

The four following reactions, where \( \eta^0 \) is the standard redox potential, occurred in the experimental system. Therefore, we quantitatively determined each output using a colorimetric determination method and gas chromatography.

\[
N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \\
2H^+ + 2e^- \rightarrow H_2 \\
C_2H_3OH + 2h^+ \rightarrow CH_3CHO + 2H^+ \\
\text{and} \\
4OH^- + 4h^+ \rightarrow 2H_2O + O_2
\]

As a result, the evolution rate of each product was estimated to be 3.76 nmol h⁻¹ (H₂), 1.20 nmol h⁻¹ (O₂), and 1.82 nmol h⁻¹ (CH₃CHO). Although \( \eta^0 (O_2/H_2O) \) was more positive than \( \eta^0 (CH_3CHO/ETO) \), oxygen evolution was clearly observed, because plasmon-induced charge separation oxidizes water efficiently, as previously discussed. Both ammonia and
hydrogen were observed at the cathode after electrolysis, because Ru is also an effective co-catalyst for hydrogen evolution [35–37]. Furthermore, the number of electrons and holes consumed by the reactions in formulae (4.1)–(4.4) indicates the balance between the cathode and the anode. Therefore, the redox reaction was confirmed to be stoichiometric. We have successfully constructed a plasmon-induced system for ammonia synthesis that responds to visible wavelengths without any external electrochemical apparatus.

In conclusion, we have constructed plasmon-induced water-splitting and ammonia synthesis systems using gold-nanostructured Nb–SrTiO3 photoelectrodes that respond to visible light. The present quantum efficiencies of hydrogen and ammonia production were estimated to be approximately 10−3% and 10−2%, respectively. Although these values are far lower than the expected efficiency, the proposed plasmon-induced artificial photosynthesis system has some advantages as follows. The redox reactions proceeded separately on both the front and back of the same Nb–SrTiO3 substrate, and the types of evolved gases were controlled by the reduction co-catalyst. Unlike molecular sensitizers, gold nanoparticles exhibit good long-term stability and their plasmon bands can be tuned to cover a large part of the solar spectrum by simply changing their shape and size. To improve the quantum efficiency, we propose that gold nanoparticles should be placed on the three-dimensional architecture of a semiconductor surface. Moreover, the interfacial structure between semiconductors and metal or reduction co-catalysts should be optimized. The Schottky barrier between the semiconductor and the co-catalyst on the cathode side should be completely removed to induce the smooth migration of electrons from the semiconductor to the reduction co-catalyst. These constitute the most important features of this system, because electrons injected into the conduction band of the semiconductor migrate to the back of the substrate to promote reduction. Thinner substrates are also considered to be better for avoiding losses owing to electron trapping in the defect level. If these proposed goals are achieved, the system could potentially be used to construct efficient and robust artificial photosynthesis systems that respond, with low chemical biases, to visible and near-infrared light.

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