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Photocatalytic Ammonia Decomposition Using Dye-Encapsulated Single-Walled Carbon Nanotubes

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Abstract: Photocatalytic ammonia decomposition to produce N_2 and H_2 was achieved using single-walled carbon nanotube (SWCNT) nanohybrids. Physical modification of ferrocene-dye-encapsulated CNTs by amphiphilic C_{60}-dendron yielded nanohybrids with a dye/CNT/C_{60} coaxial heterojunction. Upon visible light irradiation, an aqueous solution of NH_3 and dye@CNT/C_{60}-dendron nanohybrids produced both N_2 and H_2 in a stoichiometric ratio of 1:3. Action spectra of this reaction clearly demonstrated that the encapsulated dye acted as the photosensitizer, with an apparent quantum yield (AQY) of 0.22% at 510 nm (the λ_{max} of the dye). This study presents the first example of dye-sensitized ammonia decomposition and offers a new avenue for developing efficient and sustainable photocatalytic hydrogen production systems.

Keywords: photocatalyst; ammonia decomposition; dye sensitization; hydrogen evolution; carbon nanotube; fullerene

1. Introduction

To make ammonia a hydrogen carrier, its dehydrogenation reaction to produce CO_x-free hydrogen is highly anticipated [1]. Such ammonia decomposition is mildly endothermic, so it requires that temperatures higher than 773 K be applied with the most active Ru-based catalysts to obtain an appropriate H_2 production. In this context, photocatalytic ammonia decomposition that proceed at room temperature has attracted tremendous interest [2]. However, examples of photocatalytic decomposition of aqueous ammonia solutions evolving only H_2 and N_2 is limited and most of them can use not visible- but UV-light. For instance, Kudo and co-workers reported Ru-loaded ZnS showed the ammonia decomposition activity upon photoirradiation, of which wavelength was less than 350 nm [3]. Although Fe-doped TiO_2 [4] and MoS_2/N-doped graphene hybrids [5] have been described as visible and/or near-IR responsive photocatalyst for ammonia decomposition as exceptional examples, controlling active wavelength ranges was still a not-solved-problem. In this context, a new light absorber that can introduce the photocatalytic systems to convert ammonia to H_2 and N_2 is highly required.

Meanwhile we have developed photocatalytic water splitting systems using carbon nanotubes (CNTs) [6–11] and dye-encapsulated carbon nanotubes [12–15] as light absorbers. Interestingly, using CNTs as a platform for making coaxial heterojunction, we fabricated coaxal nanohybrids, CNT/C_{60} and dye@CNT/C_{60}, that exhibit efficient charge-separated-state generation followed by electron migration to co-catalyst to generate H_2 upon visible light irradiation. From the viewpoint of visible light absorbers, dye **1** [13,16] is quite interesting, because **1** was easily encapsulated into CNT by solution process to obtain **1**@CNT, of which physical modification with amphiphilic C_{60}-dendron gave **1**@CNT/C_{60}-dendron nanohybrid (Figure 1). Endohedral dye **1** shows the outstanding stability against light irradiation and as well, photosensitizing ability for water splitting, with an apparent quantum yield (AQY) reaching nearly 10% under 510 nm light irradiation [12]. Based on this background, we decided to investigate ammonia decomposition using dye-encapsulated CNT photocatalysts. In this paper, we demonstrate the decomposition of an aqueous ammonia solution into H_2 and N_2 using **1**@CNT/C_{60}-dendron nanohybrid as a photocatalyst in the presence of $RuCl_3$ under visible light irradiation at room temperature. To the best of our knowledge, this is the first example of a dye-sensitized ammonia decomposition reaction.

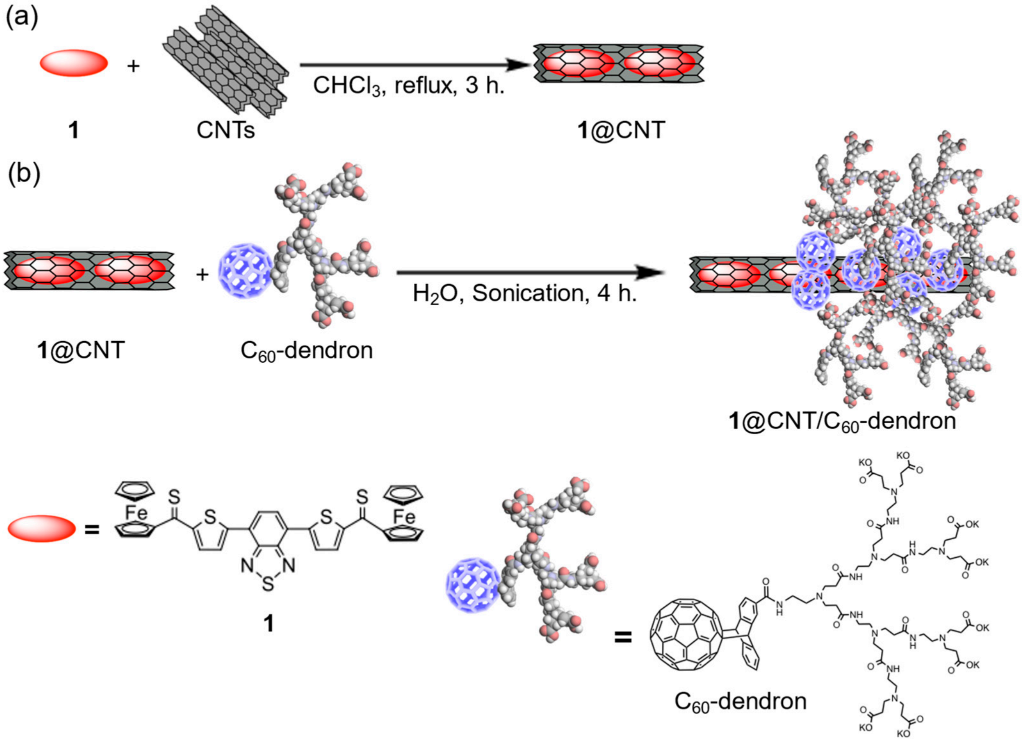

Figure 1. Fabrication of **1**@CNT/C_{60}-dendron acting as a photocatalyst.

2. Result and Discussions

To explore dye-sensitized ammonia decomposition, we synthesized **1**@CNT/C_{60}-dendron nanohybrid with a dye/CNT/C_{60} coaxial heterojunction using dye **1**, single-walled carbon nanotubes (CNTs), and amphiphilic C_{60}-dendron, as previously reported (Figure 1) [12]. In a typical run, **1** and CNTs were sonicated in chloroform for 1 h to obtain dye-encapsulated CNT, **1**@CNT. The obtained filtrate was repeatedly washed with chloroform to remove any dye remaining on the surface of CNTs. Afterward, **1**@CNT and C_{60}-dendron in water was sonicated for 4 h and centrifuged for 30 min (3000 G) to obtain a water dispersion of **1**@CNT/C_{60}-dendron, of which unadsorbed C_{60}-dendron in the dispersion was removed by dialysis. Figure 2a shows photographs of the water dispersions of CNT/C_{60}-dendron and **1**@CNT/C_{60}-dendron. It is evident that the solution turns a purplish color due to the absorption of the endohedral dye **1**. Figure 2b shows the absorption spectra of CNT/C_{60}-dendron, **1**@CNT/C_{60}-dendron, and **1**. Although the wide absorption range of CNTs from visible to near-infrared masks the absorption of dye **1**, the absorption band of **1** is included in the 450 - 600 nm wavelength range.

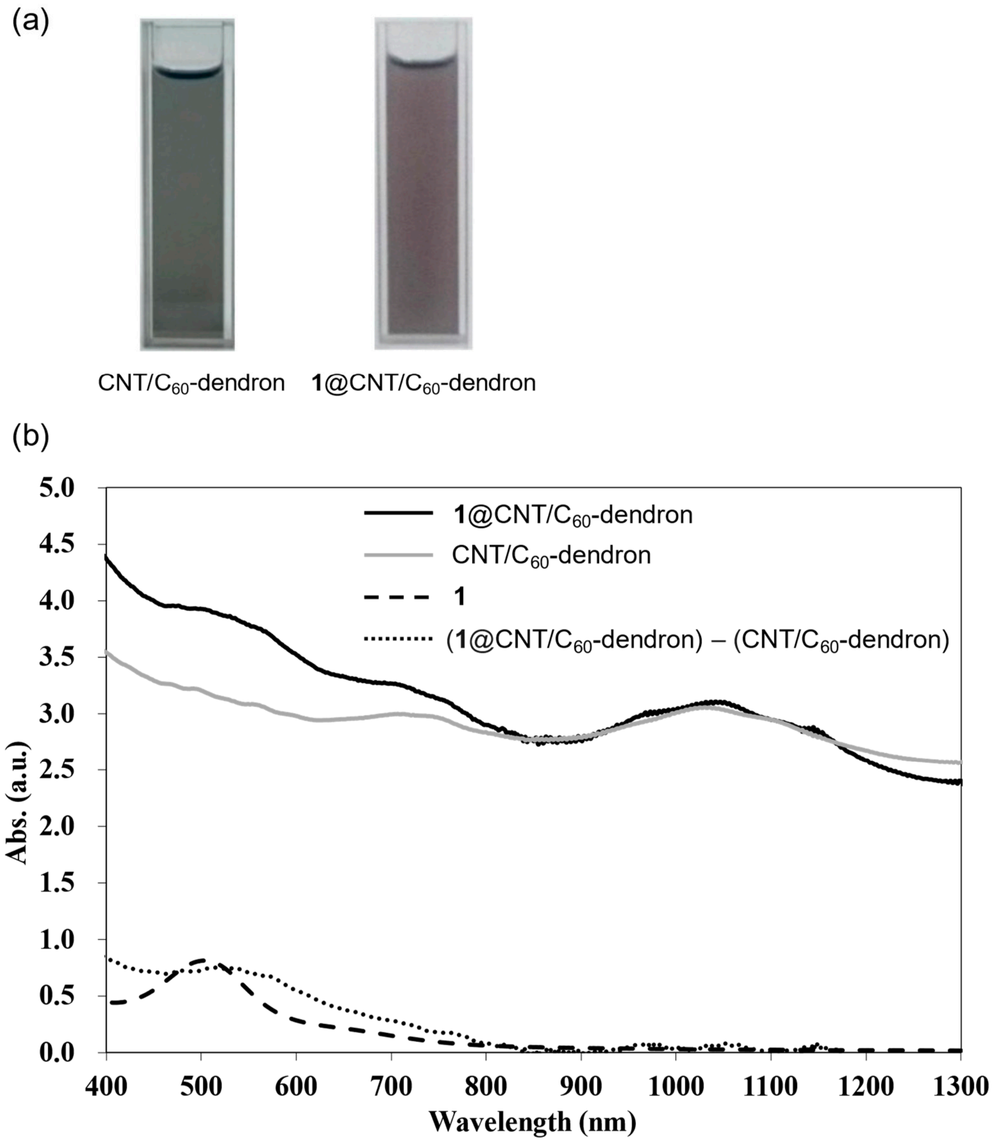

Figure 2. (a) Photograph of a water-dispersion of CNT/C_{60}-dendron (left) and **1**@CNT/C_{60}-dendron (right), (b) absorption spectra of dye **1**, CNT/C_{60}-dendron, and **1**@CNT/C_{60}-dendron in water.

Figure 3 shows the time course of H_2 and N_2 production using **1**@CNT/C_{60}-dendron as a photocatalyst. Upon visible light irradiation ($\lambda > 422$ nm), **1**@CNT/C_{60}-dendron in an aqueous ammonia solution shows both H_2 and N_2 evolution activity, of which rates are 1.8 μmol/h and 0.67 μmol/h, respectively, in the presence of $RuCl_3$. The production ratio of H_2 to N_2 was close to 3:1, suggesting that the ammonia decomposition reaction ($2NH_3 \rightarrow N_2 + 3H_2$) proceeded. The amounts of H_2 and N_2 increased linearly for 12 h, but after that a decline in activity was observed. Measuring the pH of the solution revealed that it decreased from pH 11 at the start of the reaction to pH 10 after the reaction stopped, 24 h, suggesting that the decrease in pH reduced the decomposition rate. In fact, we have observed the pH dependency of the activity where activity was decrease significantly below pH 11. We confirm that this reaction did not proceed in the dark. Hence, this process is photocatalytic reaction. Additionally, in the absence of $RuCl_3$, the ammonia decomposition reaction did not proceed. We have reported that $RuCl_3$ act as a hydrogen evolution cocatalyst in the water splitting system containing **1**@CNT/C_{60}-dendron. Therefore, it is considered that the Ru complex acts as a hydrogen production cocatalyst in this reaction system as well.

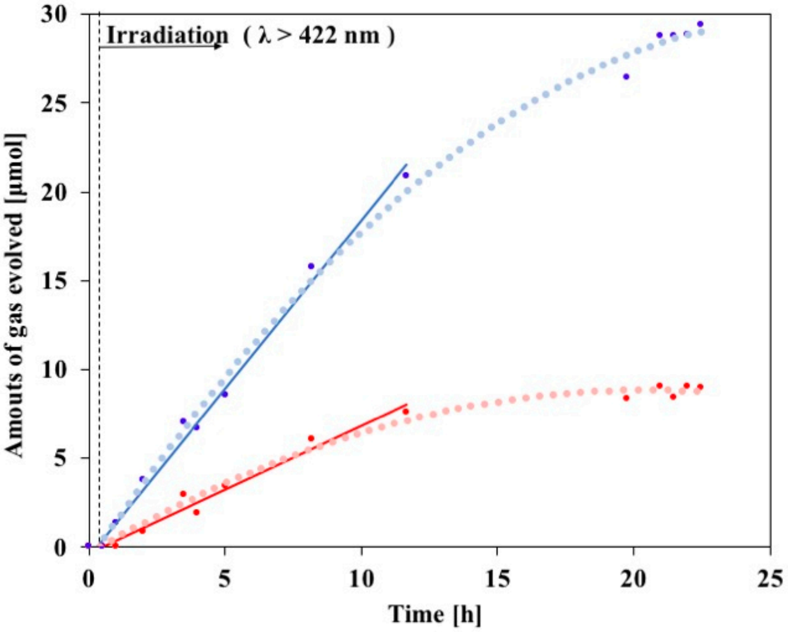

Figure 3. Time course of the H_2 (blue) and N_2 (red) evolution using **1**@CNT/C_{60}-dendron photocatalyst under irradiation with visible light (300W-Xe; λ > 422 nm, 3000 Wm^2).

To identify the light absorber in the photocatalytic system, we measured the action spectra (Figure 4). Under monochromatic light irradiation (450, 510, 550, and 650 nm), the apparent quantum yield (AQY) values derived from the hydrogen production rates were 0.047% at 450 nm, 0.22% at 510 nm, 0.042% at 550 nm, and 0.0070% at 650 nm, respectively. The variation in activity with the wavelength of the irradiation light closely matches the absorption spectrum of endohedral dye **1**. This indicates that the ammonia decomposition reaction is photosensitized by **1**. Moreover, compared to the AQY of ZnS_2, 0.21% under 340-nm-light-irradiation, **1**@CNT/C_{60}-dendron exhibits similar AQY (0.22%) under longer wavelength, 510-nm-light-irradiation.

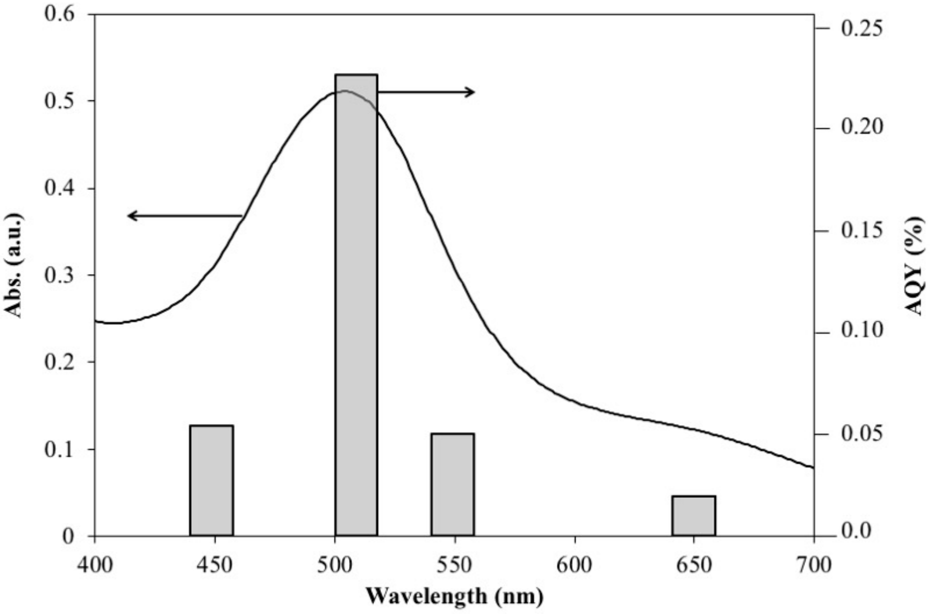

Figure 4. UV−vis spectrum of **1** in chloroform, as well as action spectra for the evolution of H_2 from H_2O using **1**@CNT/C_{60}-dendron.

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In terms of a plausible mechanism of the dye-sensitized ammonia decomposition ($NH_3 \rightarrow 1/2N_2 + 3/2H_2$), it has a ΔG° of +27 kJ/mol (0.28 eV), which corresponds to the energy in the infrared region (4.43 μm). Therefore, visible light absorption of endohedral dye **1** can provide sufficient energy for this reaction. The electrons generated by photoexcitation of **1** are utilized in the H_2 evolution via two-electron reduction of protons ($2H^+ \rightarrow H_2$) at the co-catalyst, $RuCl_3$, and the holes are utilized in the N_2 evolution via six-electron oxidation of ammonia ($2NH_3 \rightarrow N_2 + 6H^+$) at the CNT-surface. Figure 5 shows the energy level diagram for this reaction. Although the CNTs are a chirality mixture, the energy levels of the HOMO and LUMO of a representative (13,8) tube are shown. The HOMO and LUMO of the dye **1** are shown as reported in the literature. The H_2 evolution through photoinduced electron transfer from **1** to C_{60} and Ru(III) co-catalyst has already been reported in water splitting, demonstrating sufficient level of **1**'s LUMO for ammonia decomposition reaction. The energy level of the photogenerated holes on **1** is +0.80 V, which is deeper than the energy level of the HOMO of the CNT (+0.35 V), suggesting that the holes migrate to the CNT and are consumed in the oxidation reaction of NH_3. Considering the standard electrode potential for the nitrogen production reaction via the oxidation of ammonia ($N_2(g) + 6H^+ + 6e^- = 2NH_3\,(aq)$) is -0.092 V, the HOMO level of the CNT is sufficiently deep to enable nitrogen production via the oxidative decomposition of ammonia.

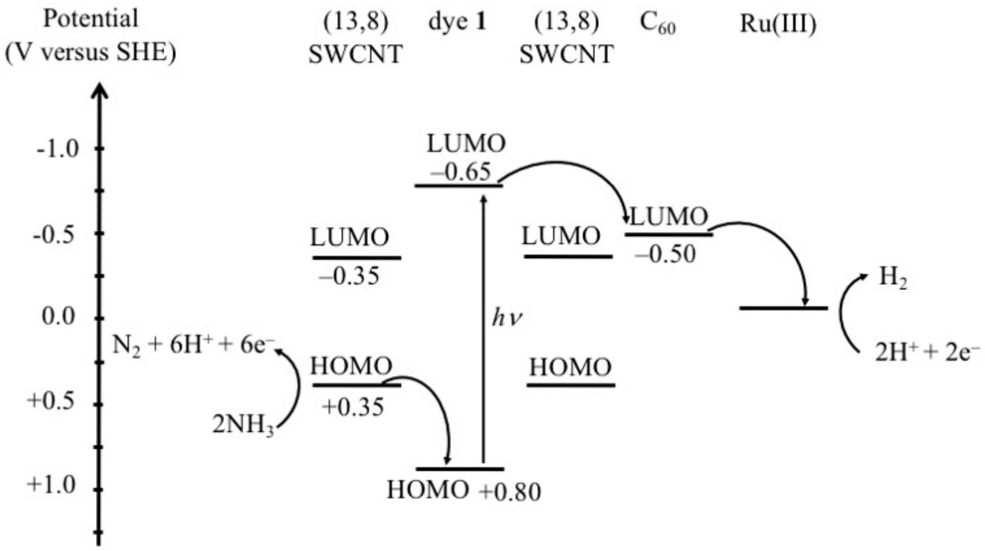

Figure 5. Energy-level diagram of the photocatalytic decomposition of NH_3 using **1**@SWCNT/C_{60}-dendron to evolute H_2 and N_2.

Figure 6 shows the time course of the ammonia decomposition reaction under simulated sunlight (AM1.5). After 26 hours, the amount of hydrogen produced reached 64.7 μmol, and the amount of nitrogen produced reached 15.5 μmol. The STH (solar-to-hydrogen) efficiency calculated from these results was 0.0011% for the ammonia decomposition reaction. The pH at the start of the measurement was 11.2, and after 26 hours, when hydrogen production stopped, the pH was 10.4. The result indicated that the ammonia decomposition reaction was stopped owing to the lowering pH of the solution. But the pH of the solution was adjusted to 11.2 by adding KOH solution and irradiation was resumed, hydrogen and nitrogen production resumed, where the ratio of N_2 and H_2 evolution rate, 0.90 and 0.30 μmol/h, respectively, was perfectly 3:1.

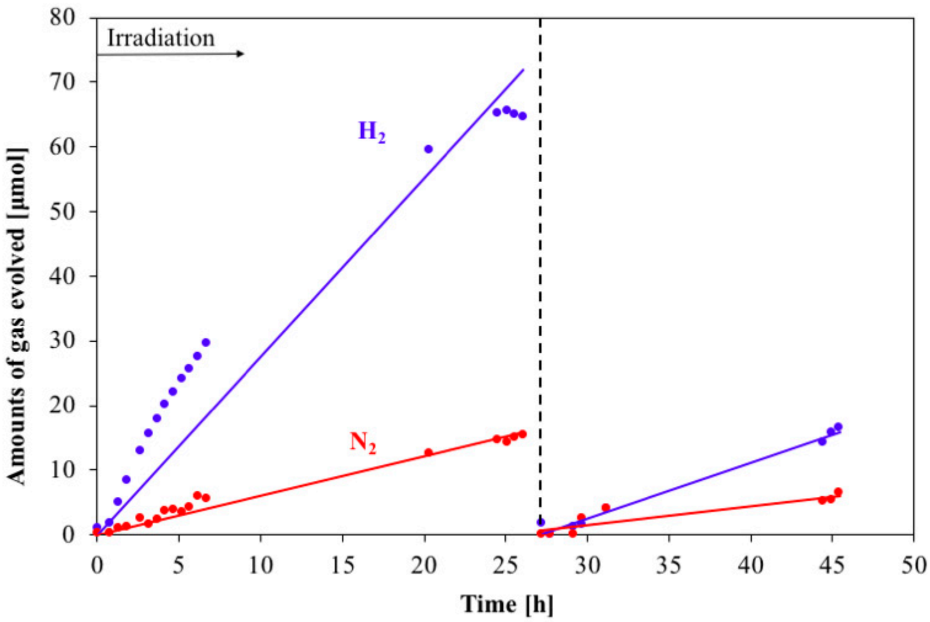

Figure 6. Time course of the H_2 (blue) and N_2 (red) evolution using **1**@CNT/C_{60}-dendron photocatalyst under irradiation with simulated sunlight (AM-1.5G; 1000 Wm^2).

3. Materials and Methods

3.1. Materials

Carbon nanotubes (CNTs), known as SO-tubes, were purchased from Meijo Nanocarbon Inc. Dye **1** was obtained from Fujifilm Wako Chemicals. All other reagents were sourced from Kanto Kagaku Co., Ltd., Sigma-Aldrich Co., and Tokyo Kasei Co., Ltd. All chemicals were used as received without further purification.

3.2. Preparation of a Stock Solution of 1@CNT/C_{60}-Dendron

Dye **1** encapsulated CNTs (**1**@CNTs) and **1**@CNT/C_{60}-dendron nanohybrids were prepared according to a previously reported procedure [12]. **1**@CNTs (1.0 mg) were added to an aqueous solution (10 mL) of C_{60}-dendron (25.5 mg, 0.01 mmol) and sonicated using a bath-type sonicator (Honda Electronics Co., Ltd., VS-D100, 110 W, 24 kHz) at 17-25 °C for 4 hours. After sonication, the suspension was centrifuged at 3000 G for 30 minutes, and the black supernatant, containing **1**@CNT/C_{60}-dendron nanohybrids and excess C_{60}-dendron, was collected. The **1**@CNT/C60-dendron was purified by dialysis for 3 days using dialysis tubing (SPECTRUM RC MEMBRANES Pro 4) to remove excess C_{60}-dendron that was not adsorbed onto the CNT surfaces. The dialysis process continued until no change in absorption at 255 nm (C_{60}'s absorption) was observed in the UV-vis spectra of the dialysate. The resulting black-colored solution of **1**@CNT/C60-dendron was then used as a stock solution.

3.3. Photocatalytic Decomposition of Ammonia Using 1@CNT/C_{60}-Dendron

To the stock solution of **1**@CNT/C_{60}-dendron (0.75 mL), $RuCl_3$ (6.3 mg, 30 mmol) was added and stirred for 30 minutes to load the Ru(III) co-catalyst onto the shell of **1**@CNT/C_{60}-dendron. The resulting solution of **1**@CNT/C60-dendron/Ru(III) was then added to an aqueous NH_3 solution (149.25 mL), prepared by mixing aqueous NH_3 (1 mL, 13.8 M) with deionized water (148.25 mL). The pH of this solution was 11. The mixture was degassed for five cycles and purged with Ar in a Pyrex reactor. Under vigorous stirring, the solution was irradiated with a 300 W Xenon arc lamp (Ushio model UXL-500 W) through bandpass filters (λ = 450, 510, 550, 650, and > 422 nm: ASAHI SPECTRA CO, M.C.). After the designated reaction time, the cell containing the reaction mixture was connected to a gas chromatograph (Shimadzu, TCD, molecular sieve 5A: 2.0 m × 3.0 mm, Ar carrier gas) to measure the amounts of H_2 and N_2 evolved in the gas phase above the solution. The apparent quantum yield (AQY) was defined as follows: AQY = (number of H_2 molecules generated × 2) / (number of photons absorbed). The AQY was evaluated by measuring the change in the power of the transmitted light using a power meter (Photo-radiometer Model HD 2302.0 coupled with an irradiance measurement probe LP 471 RAD, with an exposure window diameter of 1.6 cm) placed behind the cell, parallel to the irradiation cell face.

4. Conclusions

In conclusion, the production of nitrogen and hydrogen via dye-sensitized ammonia decomposition was successfully proceeded. By utilizing carbon nanotubes as a platform, we constructed **1**@CNT/C_{60} coaxial heterojunctions, enabling the use of endohedral dye **1** as a photosensitizer. This approach allows for the construction of ammonia decomposition systems employing various dyes. We do not satisfy with the current values of AQY and STH. And we feel these low values might be attributed to the low efficiency of the six-electron oxidation reaction of ammonia. Now we attempt to investigate the mechanism of ammonia oxidation and improve the molecular design of endohedral dyes to enhance the activity of the dye-sensitized ammonia decomposition reaction. This research aims to pave the way for more efficient and practical systems for sustainable hydrogen production from ammonia using solar energy.

Author Contributions: Conceptualization, Y.T.; methodology, K.Y.; validation, K.M.; investigation, K.Y.; resources, K.Y.; data curation, T.T.; writing—original draft preparation, K.Y. and Y.T.; writing—review and editing, Y.T. and T.T.; supervision, project administration, and funding acquisition, Y.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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