Photocatalysis: A Possible Vital Contributor to the Evolution of the Prebiotic Atmosphere and the Warming of the Early Earth

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Abstract: The evolution of the early atmosphere was driven by changes in its chemical composition, which involved the formation of some critical gases. In this study, we demonstrate that nitrous oxide (N\textsubscript{2}O) can be produced from Miller’s early atmosphere (a mixture of CH\textsubscript{4}, NH\textsubscript{3}, H\textsubscript{2}, and H\textsubscript{2}O) by way of photocatalysis. Both NH\textsubscript{3} and H\textsubscript{2}O were indispensable for the production of N\textsubscript{2}O by photocatalysis. Different conditions related to seawater and reaction temperature are also explored. N\textsubscript{2}O has a strong greenhouse gas effect, which is more able to warm the Earth than other gases and offers a reasonable explanation for the faint young Sun paradox on the early Earth. Moreover, the decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2} can be boosted by soft irradiation, providing a possible and important origin of atmospheric O\textsubscript{2} and N\textsubscript{2}. The occurrence of O\textsubscript{2} propelled the evolution of the atmosphere from being fundamentally reducing to oxidizing. This work describes a possible vital contribution of photocatalysis to the evolution of the early atmosphere.

Keywords: origin of O\textsubscript{2}; nitrous oxide; faint young sun paradox; photocatalysis; early earth

1. Introduction

The Earth experienced a fainter Sun in its early stages. In the ancient Archean eon, the early Earth received only 76–83% of the energy from the Sun that it does today [1]. As a consequence, the Earth would have become covered with ice if the greenhouse effect and surface albedo were the same as in the present. However, geological evidence has uncovered the presence of liquid H\textsubscript{2}O on the early Earth’s surface, and the Archean may have been warmer than today, as we are currently in a period of glaciation [2,3]. This is known as “the faint young Sun paradox” [4,5]. To date, many hypotheses have been proposed to resolve this paradox, but there is still no clear conclusion at present.

The chemical composition change of the Earth’s early atmosphere played a vital role in the atmospheric evolution, climate change, and the evolution of the early Earth to the modern Earth suited for life. For instance, a high concentration of greenhouse gases (CH\textsubscript{4} and CO\textsubscript{2}) has been suggested to help to resolve “the faint young Sun paradox”. However, geological evidence has demonstrated that the concentration of these two greenhouse gases in the early atmosphere could not have been high enough to satisfy this paradox [6]. Alternatively, Airapetian et al. proposed that the energetic particles from an active young Sun penetrated the atmosphere and converted N\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2} to N\textsubscript{2}O and hydrogen cyanide (HCN) [7]. It has been found that the greenhouse effect of N\textsubscript{2}O (298 GWP) is much stronger than those of CH\textsubscript{4} (82.5 GWP) and CO\textsubscript{2} (1 GWP) [8,9], which means that N\textsubscript{2}O has a much stronger greenhouse effect, and has more potential to have warmed the early Earth. Moreover, Nna-Mvondo et al. found that oxynitride (NO and N\textsubscript{2}O) can be produced in a mimetic Hadean and Archean atmosphere (CO\textsubscript{2}-N\textsubscript{2} mixture) by lightning and coronal discharge [10]. Nevertheless, low oxynitride yield by this means and light-induced decomposition would have limited N\textsubscript{2}O accumulation on the early Earth. Therefore, there
is possibly an overlooked process for the stable and abiotic mass production of N\textsubscript{2}O, which may be key to explaining “the faint young Sun paradox”.

In addition to the Earth’s early temperature, the origin of O\textsubscript{2} is another mystery of the evolution of the atmosphere. It has been proven that the O\textsubscript{2} level of the early Earth changed substantially over geological time [11]. For example, molybdenum isotopes found in the rocks of South Africa indicate the possible emergence of substantial free O\textsubscript{2} in shallow marine environments approximately 3 Gyr [12]. Some models have demonstrated that “O\textsubscript{2} oases” may have been created before the Great Oxidation Event (GOE) [13,14]. The origins and rise of atmospheric O\textsubscript{2} on the early Earth have aroused wide interest. O\textsubscript{2}-producing cyanobacteria or other green non-sulfur bacteria are considered to have promoted the evolution of the early Earth’s atmosphere to an O\textsubscript{2}-rich atmosphere [15]. The recent results of CO\textsubscript{2} photodissociation experiments may have implications for non-biological O\textsubscript{2} production in a CO\textsubscript{2}-heavy atmosphere [16,17]. Since N\textsubscript{2}O can be decomposed into O\textsubscript{2} and N\textsubscript{2} through thermocatalysis or under soft irradiation [18,19], atmospheric O\textsubscript{2} could be related to the level of N\textsubscript{2}O if the large-scale generation of N\textsubscript{2}O was possible on the early Earth. Moreover, some studies have also reported the decomposition of N\textsubscript{2}O into O\textsubscript{2} and N\textsubscript{2} from the perspective of photodissociation dynamics [20,21].

Different sources of energy, such as ultraviolet light, electrical discharges, radioactivity, and volcanoes, have been examined in many experimental studies on prebiotic chemistry [22]. Among these energy sources, solar energy is the most powerful and continuous source of energy. Photocatalysis can use abundant solar energy to achieve solar-to-chemical energy conversion, and has attracted widespread research interest in recent decades [23–25]. Additionally, the radiation level on the early Earth was several orders of magnitude higher in the short wavelength range than the current level at the Earth’s surface [26,27]. It could be assumed that semiconductor minerals turned the surface of the early Earth into a photoreactor under the conditions of high ultraviolet irradiation and the early Earth’s thin atmosphere [28]. Interestingly, Harald et al. obtained a mixture of amino acids from an NH\textsubscript{3} solution with CH\textsubscript{4} over a Pt/TiO\textsubscript{2} photocatalyst under irradiation from an Xe lamp [29]. Although great efforts have been made to account for the evolution of the early Earth and the origin of O\textsubscript{2}, few hypotheses have focused on the contribution of photocatalysis which may have played an important role in these processes [30,31].

In this work, we present a feasible photocatalytic way to efficiently produce N\textsubscript{2}O from a mimicked early reducing atmosphere using natural semiconductor materials (i.e., TiO\textsubscript{2}) under light irradiation. TiO\textsubscript{2}, one of the most widely used and chemically stable photocatalysts, is abundant on Earth, as well as on other planets such as Mars [32]. Herein, we used TiO\textsubscript{2} for the photocatalytic conversion of the mimicked early reducing atmosphere (CH\textsubscript{4}, H\textsubscript{2}, H\textsubscript{2}O, and NH\textsubscript{3}) applied in Miller’s experiments. The photocatalytic oxidation of NH\textsubscript{3} to N\textsubscript{2}O may be a feasible and important way to understand the chemical evolution of the early Earth. Since N\textsubscript{2}O has a strong greenhouse effect, the steady generation of N\textsubscript{2}O could have caused a warm early Earth, and the decomposition of N\textsubscript{2}O by solar light may have produced abiogenic O\textsubscript{2} for the early Earth. Furthermore, we attempt here to explain the two primary enigmas (the faint young Sun paradox and the origin of atmospheric O\textsubscript{2}) of the early Earth.

2. Results and Discussion
2.1. The Faint Young Sun Paradox

A mixture of gases (CH\textsubscript{4}, H\textsubscript{2}, H\textsubscript{2}O, and NH\textsubscript{3}), similar to that used in Miller’s experiment, was employed to mimic the early reducing atmosphere. Among these gases, NH\textsubscript{3} is considered a probable part of the composition of the early atmosphere [33–35], which may come from the degasification of the Earth or have been generated from nitrate through denitrification [34,36,37]. It has been noted that the ammonium concentration of Paleoarchean metasedimentary biotite grains reached up to several hundred ppm [38], which raises the possibility of a NH\textsubscript{3}-rich atmosphere on the early Earth. Nitrogen isotope ratios have offered evidence for the existence of the oldest known alkaline lake system which may
have provided alkaline conditions for the volatilization of NH$_3$ gas [39]. Therefore, NH$_3$
may have been a sufficient reactant for the production of N$_2$O on the early Earth.

Solar light is continuous and had high ultraviolet irradiance on the early Earth, which
allows it to meet the needs of photocatalytic reactions [27,40]. If N$_2$O can be effectively
produced from the primitive atmosphere (including NH$_3$ and H$_2$O) with inexhaustible solar
energy, a possible explanation could be offered to address the faint young Sun paradox.
N$_2$O is generally considered to primarily enter the atmosphere as a byproduct of biological
nitrification and denitrification [33,41]; oceanic O$_2$ restricted the concentration of N$_2$O on
the early Earth [42] because N$_2$O is rapidly photodissociated at lower atmospheric O$_2$
levels. In this work, we present experimental evidence that N$_2$O can be generated from
and accumulated in a mimicked early reducing and anoxic atmosphere (NH$_3$, H$_2$O) via
photocatalysis. Thus, the concentration of N$_2$O need not be dependent on O$_2$ levels or
biological enzymes.

For the simplification and reliability of the reaction system, commercial TiO$_2$ powder
was chosen instead of natural semiconducting minerals due to the lower symmetries
and additional complexities of the latter. The commercial TiO$_2$ powder was evaluated
using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM),
diffusion reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS)
(Figures S1 and S2). The crystal phase of the applied TiO$_2$
was anatase, and its average
particle size was approximately 5 nm. Our experiment was performed in an airtight silica
tube (Figure 1) containing mixed gases, water, and photocatalyst. The mixed gases mimic
the primitive atmosphere (CH$_4$, H$_2$, and NH$_3$), as used in Miller’s experiments [43], and
the aqueous solution represents the primitive ocean. The gas composition was monitored
using a Fourier transform infrared spectrometer (FTIR) through the CaF$_2$ window. After
5 days of photocatalytic reaction, obvious double peaks were observed at around 2238
and 2213 cm$^{-1}$, corresponding to N$_2$O [44] (Figure 2a). The generation of N$_2$O indicated
that both NH$_3$ and H$_2$O were indispensable for the reaction; thus, we used NH$_3$ and H$_2$O
as reactants in the subsequent experiments. As expected, N$_2$O was can be also produced
(Figure 2b), and the amount of N$_2$O gradually increased day by day via photocatalytic
reaction (Figure 3a) with the photocatalyst and light illumination. In this reaction, NH$_3$
is oxidized to N$_2$O and water is reduced to H$_2$ (2NH$_3$ + H$_2$O $\rightarrow$ N$_2$O + 4H$_2$). The amount of
H$_2$ is shown in Figure S3. Additionally, we detected the concentration of NO$_3^-$ and NO$_2^-$
in the liquid phase (Figure S4) and no obvious signal was observed, which indicates N$_2$O
is the single oxidative product of NH$_3$. Meanwhile, even when the reaction temperature
was adjusted to 3 $^\circ$C, the formation of N$_2$O still proceeded (Figure 2c) (note that negative
double peaks around 2348 cm$^{-1}$ are attributed to the fluctuation of CO$_2$ concentration in
the air (outside the reaction tube), which did not influence the reaction). Furthermore, we
also investigated simulated present-day seawater (0.462 M NaCl, 1.3 mM MgSO$_4$, 0.04 M
MgCl$_2$, and 6.8 mM MgBr$_2$) instead of pure water for photocatalytic N$_2$O production. After
7 days of irradiation, obvious double peaks were observed at around 2238 and 2213 cm$^{-1}$,
corresponding to N$_2$O (Figure 2d) with no new peaks observed. Moreover, the amount
of N$_2$O evolution was further detected using gas chromatography [45] (Figure 3b). The
highest evolution rate of N$_2$O was measured at approximately 20 $\mu$mol per day. For
comparison, in the absence of a catalyst or light irradiation, the target product (N$_2$O) was
nearly undetectable in the control experiments (Figure 4).
Figure 1. Schematic drawing of the experimental apparatus.

Figure 2. FTIR spectra of gas phase before irradiation and after 5 days of irradiation. Reaction gas: (a) CH$_4$, H$_2$, H$_2$O, and NH$_3$; (b) reaction gas: NH$_3$ and H$_2$O; reaction conditions: 10 mL H$_2$O, ambient temperature; (c) reaction gas: NH$_3$ and H$_2$O; reaction conditions: 10 mL H$_2$O, 3 °C; (d) reaction gas: NH$_3$ and H$_2$O; reaction conditions: 10 mL simulated seawater, ambient temperature.
The rate of production of N$_2$O by photoreduction was approximately $4 \times 10^{11}$ g yr$^{-1}$ (grams per year), which is comparable to the N$_2$O emission estimated from lightning [46,47]. Table 1 shows the geochemical data of the modern Earth and terrestrial planets [46,47], and the rate of production of N$_2$O by photoreduction was approximately $4 \times 10^{11}$ g yr$^{-1}$ (grams per year), which is comparable to the N$_2$O emission estimated from lightning [46,47].

Owing to the limited gas tightness and vacuum degree of the experimental apparatus, the effect of ambient O$_2$ could not be entirely excluded in our experiments. To verify that the oxygen atoms in N$_2$O originated from H$_2$O, $^{18}$O-labeled H$_2$O was added into the reaction system. Table 1 shows the ratios of $^{18}$O in $^{18}$O-labeled H$_2$O and N$_2$O. The $^{18}$O content of the generated N$_2$O reached 0.405 atom%, which was apparently higher than the natural abundance (0.2 atom%). This proves the feasible transfer of oxygen atom from H$_2$O to N$_2$O, and approximately 16% of the N$_2$O in our system was from the reduction of H$_2$O due to the competition of ambient O$_2$.

**Table 1.** Oxygen isotopic compositions of N$_2$O and $^{18}$O-labeled H$_2$O.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amplt 44/28</th>
<th>$\delta^{18}$O$_{VSMOW}$</th>
<th>AT% $^{18}$O/$^{16}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{18}$O-labeled H$_2$O</td>
<td>486</td>
<td>7209.5</td>
<td>1.4826</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>126</td>
<td>1018.3</td>
<td>0.4051</td>
</tr>
</tbody>
</table>

To estimate N$_2$O production by photocatalysis on the early Earth, we assumed that the irradiated surface area was equal to the internal cross-section of the tube (8 cm$^2$); therefore, the reaction rate on the irradiated surface area was 25 mmol/m$^2$/day. Given that the land area of the early Earth was similar to that of the modern Earth (149 million square kilometers) and that the proportion of TiO$_2$ area was approximately 1% according to the geochemical data of the modern Earth and terrestrial planets [46,47], the rate of production of N$_2$O by photoreduction was approximately $4 \times 10^{11}$ g yr$^{-1}$ (grams per year), which
was much larger than that predicted using the discharge method \((9 \times 10^7 \text{ g yr}^{-1})\) [10]. Additionally, we also carried out a gas–solid photocatalytic reaction experiment in which TiO\(_2\) powder was deposited on a glass substrate placed above the surface of the water. The reaction rate on the irradiated surface area was \(10 \text{ mmol/m}^2/\text{day}\) (Figure 5) and the corresponding estimated production of N\(_2\)O was, thus, approximately \(2 \times 10^{11} \text{ g yr}^{-1}\), which is a potential origin of greenhouse gas able to offset reduced insolation in the early Earth and maintain a warm climate. Additionally, since N\(_2\)O has a stronger greenhouse effect than CH\(_4\) or CO\(_2\) [48], a lower N\(_2\)O concentration would have been needed to warm the early Earth. Crucially, the removal of N\(_2\)O from the atmosphere is much lower than that of CH\(_4\), given that the steady-state lifetime of N\(_2\)O is approximately 120 years. Less than 1% of atmospheric N\(_2\)O is removed annually from the atmosphere, primarily by photolysis and oxidative reactions in the stratosphere [48]. Therefore, it is reasonable to assume that over geological time, with abundant energy sources and sufficient reactant, atmospheric N\(_2\)O may have created an insulating layer for the Earth, which may have helped to maintain liquid H\(_2\)O on the early Earth and stopped cosmic rays from reaching the Earth at the same time.

![Figure 5](image-url)

**Figure 5.** (a) FTIR spectra of the gas-phase mixture over 48 h of photocatalytic reaction. (b) The evolution rate of N\(_2\)O with TiO\(_2\) and light (red line), and without any catalyst (black line), without light (blue line). Reaction conditions: 30 mg catalyst deposited on a glass substrate (2 cm \(\times\) 2 cm), NH\(_3\), 10 mL H\(_2\)O, ambient temperature.

2.2. The Possible Origin of Atmospheric O\(_2\)

Molecular oxygen has played an indispensable role in transforming our planetary environment. Its presence in the atmosphere and oceans has also induced planetary-scale interactions between the biosphere and the environment, leading to the Earth’s system having crossed irreversible thresholds to reach its modern state. Rare earth element analyses of limestones and deep-water iron-rich sediments have shown that shallow water was oxygenated, whereas the adjacent deeper waters were not [14,49]. Regardless of the arguments raised by some studies that UV radiation would limit the expansion of cyanobacteria [50], the possible existence of “Archean cyanobacteria” could account for the oxygenation of shallow water [13,51,52]. The record of redox-sensitive trace-metals and C and S contents in black shales indicates that ocean ventilation on a global scale was delayed until later in the Cambrian with regard to rising oxygen levels in the atmosphere [53]. Notably, N\(_2\)O can be decomposed under solar light into O\(_2\) and N\(_2\) through thermocatalysis and photocatalysis [18,19,54], which may be an important origin of non-biological O\(_2\) on the early Earth. Moreover, the photocatalytic generation and photodecomposition of N\(_2\)O can increase the O\(_2\) level in shallow water but not in deep water, as deep water’s lack of solar light cannot satisfy the conditions of photocatalytic reaction. This hypothesis posits that an increase in the oxygen content of shallow water was physiologically necessary for the emergence of large, highly energetic animals [55]. Although these findings are only preliminary, they still add evidence for the existence of N\(_2\)O and O\(_2\).
Furthermore, it has been widely reported that the decomposition of N$_2$O gas to N$_2$ and O$_2$ can be induced by light. To our delight, previous studies have revealed the isotope fractionation of nitrogen atoms in the upper atmosphere and ascribed it to the ultraviolet (UV) photodissociation dynamics of N$_2$O. N$_2$O also has a broad absorption band that peaks at 182 nm, which means that it can absorb UV; the window of solar radiation occurs in the red wing of this band [56,57]. Moreover, the Gibbs free energy change ($\Delta G$) of the decomposition of N$_2$O is $-100$ KJ, which means this reaction can react spontaneously. Based on these theories, we explored the decomposition of N$_2$O under solar light with TiO$_2$. To explore the significance of light and catalysis, we also removed TiO$_2$ and light during photocatalytic N$_2$O decomposition. Owing to the limited gas tightness and vacuum degree of the experiment apparatus, the effect of the surrounding O$_2$ could not be entirely rejected, so we only detected the concentrations of N$_2$O and N$_2$. Furthermore, before irradiation, we maintained the pressure of the tube at 1 bar to minimize gas exchange with the air outside the tube. As briefly shown in Figure 6a, the concentration of N$_2$O gradually decreased with the extension of illumination time, whereas the corresponding N$_2$ showed positive growth. To determine the effects of the photocatalyst and light, we carried out the N$_2$O decomposition experiment with the participation of TiO$_2$. As exhibited in Figure 6b, N$_2$O was smoothly decomposed into N$_2$ and O$_2$ with light, even without the assistance of TiO$_2$. However, it was difficult for N$_2$O to decompose in the dark because of the inhibitive high reaction energy of N$_2$. Instead, the reaction energy decreased dramatically, contributing to the decomposition of N$_2$O in the presence of photoexcited or excess electrons on the TiO$_2$ surface. Simultaneously, we found that the evolution rate of N$_2$O with TiO$_2$ and light became slower after approximately 10 h of irradiation (Figures 3b and 5b). This indicates that the N$_2$O began to decompose when the concentration of N$_2$O reached a certain value, which is in agreement with our assumption of the decomposition of N$_2$O into O$_2$ and N$_2$.

The physical and chemical properties of the reactants and photocatalyst can support our proposed model of nitrogen cycling. Firstly, ammonia in liquid water profoundly depresses the freezing point of the mixture. Some studies have also shown evidence of liquid water temperatures at the Earth’s surface using the dating of sedimentary rocks which were laid down under water [52,58]. These conditions described by these theories could provide sufficient reactants (H$_2$O and NH$_3$) for the photocatalytic production of N$_2$O. Meanwhile, UV radiation would also provide a limitless energy source for the photocatalytic reaction without destroying the photocatalyst. Crucially, it is worth noting that throughout the production of N$_2$O, even after 30 h irradiation, the TiO$_2$ still exhibited perfect photocatalytic activity. Moreover, TiO$_2$ is considered a natural semiconductor material that is abundant on Earth, as well as on other planets such as Mars. Therefore,
a perfect correlation between the early atmosphere and the possible origin of O2 can be formed (Figure 7). The sun, along with TiO2, could provide continuous conditions for the early atmosphere to produce N2O and, simultaneously, to decompose N2O into N2 and O2. Accordingly, based on the current evidence outlined above, we conjecture the possible origin of O2 from the decomposition of N2O, which could be an important step for the chemical evolution of the early atmosphere to the modern atmosphere.

![The early Earth](image)

**Figure 7.** Sketch of the possible primary nitrogen flow on the early Earth.

3. Materials and Methods

3.1. Chemicals

Titanium dioxide (TiO2, anatase), magnesium sulfate (MgSO4), magnesium chloride (MgCl2), and magnesium bromide (MgBr2) were obtained from Aladin (Shanghai, China). Sodium chloride (NaCl) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All chemical reagents used in this work were of analytical grade and used as received without further purification or treatment. Pure (99.99%) reaction gases (NH3, CH4, N2O, and H2) were purchased from Xinghang Gas Co., Ltd. (Fuzhou, China). (and used under the control of flowmeters.

3.2. Characterization

The composition of the gas-phase mixture in the cell was monitored using a Thermo Scientific Nicolet IS50 FT-IR spectrometer (Waltham, MA, USA) equipped with a KBr beam splitter and a DTGS/KBr detector. For each spectrum, 64 scans were accumulated and measured with a resolution of 0.02 cm⁻¹ at a range of 1100 to 4000 cm⁻¹. X-ray diffraction data of TiO2 powder were collected using a Bruker D8 advance X-ray diffractometer (Billerica, MA, USA) (Cu Kα1 irradiation, λ = 1.5406 Å). UV-vis diffuse reflectance spectra were obtained using a Varian Cary 500 UV-Vis-NIR spectrometer with BaSO4 as a reflectance standard (Palo Alto, CA, USA). The morphology of the samples was obtained using a scanning electron microscope (SEM) (JSM-6700F, Tokyo Akishima, Japan) and a TECNAI F30 transmission electron microscope (TEM, Hillsboro, OR, USA). X-ray photoelectron spectroscopy (XPS) analysis of TiO2 was carried out using monochromatic Al Ka lines and Physical Electronics Quantum 2000 Scanning Esca Microprobe (VG, Madison, WI, USA). The produced N2O was detected using a gas chromatograph (Agilent 7820A, Santa Clara, CA, USA) equipped with a packed molecular sieve column (CBP-PSN.A) and nitrogen as a carrier gas.
3.3. Photocatalytic Reaction

For the N\textsubscript{2}O evolution experiment, a 380 mL (40 cm in long, 3.2 cm in diameter) quartz glass tube equipped with CaF\textsubscript{2} windows was used (Figure S1). TiO\textsubscript{2} (30 mg) was dispersed in 10 mL deionized water or simulated seawater (10 mL, 0.462 M NaCl, 1.3 mM MgSO\textsubscript{4}, 0.04 M MgCl, 6.8 mM MgBr\textsubscript{2}) and then poured into the tube. Before light irradiation, the cell was evacuated and refilled with the reaction gas (flow rate, 20 mL/min) several times to remove air inside the tube and finally filled with reaction gas to reach a pressure of one bar. The tube was then sealed and kept at the appropriate reaction temperatures (3 °C or room temperature). The sealed tube was irradiated using a 300 W Xe lamp. The composition of the gas-phase mixture was analyzed using high-resolution Fourier transform infrared spectroscopy (FTIR). In the gas–solid reaction experiment, 30 mg TiO\textsubscript{2} was dispersed in deionized water (5 mL) under ultrasonic stirring. The TiO\textsubscript{2} suspension was then deposited on half of a glass substrate (2 cm × 2 cm), and dried at 60 °C overnight. Finally, the glass substrate was placed into the quartz glass tube with the TiO\textsubscript{2}-loaded part of the substrate above the surface of water.

The decomposition of N\textsubscript{2}O was performed in the quartz glass tube at room temperature. The reactor was evacuated and purged with N\textsubscript{2} (flow rate, 20 mL/min) several times and finally filled with N\textsubscript{2}O (flow rate, 30 mL/min) and N\textsubscript{2} (flow rate, 60 mL/min) to reach a pressure of one bar. The tube was then sealed and irradiated using a 300 W Xe lamp for several days. The composition of the gas-phase mixture was analyzed using gas chromatography [45]. The gas–solid reaction experiments were performed using the same method as above (N\textsubscript{2}O evolution experiment), except that the reaction tube was filled with N\textsubscript{2}O and N\textsubscript{2}.

3.4. Isotope Ratio Mass Spectrometer

The ratio of $^{18}$O-labeled H\textsubscript{2}O was evaluated using an isotope ratio mass spectrometer (Delta V Advantage, ThermoFisher, Waltham, MA, USA) equipped with an elemental analyzer (FLASH EA 1112) and a ConFlo III versatile interface. The $^{18}$O content of the generated N\textsubscript{2}O was investigated using a stable isotope ratio mass spectrometer (Mat253, ThermoFisher, Waltham, MA, USA) equipped with a multipurpose online gas preparation instrument (GasBench II, ThermoFisher, Waltham, MA, USA containing a PoraPlotQ chromatographic column (30 m × 0.32 mm) and a GC autosampler (CombiPAL, CTC).

4. Conclusions

In summary, this study revealed a geochemical pathway for the photocatalytic conversion of NH\textsubscript{3} and H\textsubscript{2}O to N\textsubscript{2}O using a mimicked early reducing atmosphere, providing feasible evidence for the possible transformation of a NH\textsubscript{3}-rich atmosphere to a N\textsubscript{2}O-rich atmosphere on the early Earth. A N\textsubscript{2}O-rich atmosphere would have been more suitable to warm the Earth and provides a favorable way of solving the faint young Sun paradox. Moreover, the photodecomposition of N\textsubscript{2}O to N\textsubscript{2} and O\textsubscript{2} may have been an important step in the chemical evolution of the reducing atmosphere to the modern atmosphere. This work offers a possible new insight into the contribution of photocatalysis in the chemical evolution of the early atmosphere, which has crucial implications for understanding the modern Earth system.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13091310/s1, Figure S1: (a) XRD pattern of TiO\textsubscript{2} and JCPDS standard card (21-1272) [59]; (b) TEM image of TiO\textsubscript{2}. (Inset shows the HRTEM of TiO\textsubscript{2}, where lattice fringes with a spacing of 0.35 nm correspond to the (101) plane of TiO\textsubscript{2} [60].); Figure S2: (a) UV-Vis diffusion reflectance spectrum (DRS) of TiO\textsubscript{2}. (Inset: a value of 3.34 eV was observed for the band gap of TiO\textsubscript{2} between the (F(R)hv)$^{1/2}$ and E plots.); (b) XPS survey of commercial TiO\textsubscript{2} [61]; (c) Ti 2p lines and fit. The peak at 458.6 eV fits to Ti\textsuperscript{4+}, which is attributed to Ti-O in the TiO\textsubscript{2} [62]; (d) O 1s lines and fit; Figure S3: The production of H\textsubscript{2} and N\textsubscript{2}O with TiO\textsubscript{2} and light after 5 days illumination; Figure S4: Comparison of the reaction liquid ion chromatogram after irradiation (black line) and standard ion chromatogram (red line) of NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-}. 


Author Contributions: C.H. presented the ideas in the manuscript. C.C. and F.X. conducted experiments. C.C., Q.W. and W.S. analyzed the results. C.C. and F.X. wrote the manuscript with revision from C.H. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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