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Light intensity responsive changes of products in photocatalytic reduction of nitrous acid on a Cu-doped covalent triazine framework/TiO₂ hybrid

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Abstract: In the design of solar-energy conversion electrochemical systems, it is important to consider that natural sunlight fluctuates. By taking nitrous acid photoreduction as an example, the present work has shown that the reaction pathway, and hence the reaction products, dynamically responded to the variation of light intensity. Under irradiation, the photooxidation of methanol (as sacrificial agent) on TiO₂ and the reduction of HNO₂ on Cu-modified covalent triazine framework (Cu-CTF) were electrically coupled, which led to the photoreduction of HNO₂ without an external bias. The dominant reaction product changes from N₂O to NH₄⁺ with an increase in the light intensity. The operating potential also shifted negatively (or positively) when the light intensity was increased (or decreased). These results indicate that a change of the reaction pathway was triggered by a change of the operating potential of the Cu-CTF catalysts under varying light intensity. Such a light-intensity dependent change of the reaction pathway is particularly important in systems that use photoresponsive electrodes and where multiple products can be obtained, such as the solar-driven reduction of carbon dioxide and nitrogen oxides.

Introduction

Light-driven conversion of chemical substances has attracted much attention with respect to the photogeneration of valuable chemicals and the photodegradation of pollutants.^[1-4] Direct photochemical energy conversion can be achieved through the use of photocatalysts or photoelectrodes. In both cases, appropriate electron transfer co-catalysts that accelerate a target reaction must be loaded on the semiconductor particles and/or electrode.^[5-8] In most cases, materials that are already known to be active as electrocatalysts are used as co-catalysts. For example, platinum and iridium oxide, which are excellent electrocatalysts for hydrogen and oxygen generation reactions, respectively, are widely used as co-catalysts for water splitting with photocatalysts or photoelectrodes.^[9-11] In electrocatalytic reaction systems that can generate multiple chemical species, the composition of the reaction products is generally dependent on the electrode potential.^[12-15] This is because the stability of the reaction intermediate on the electrocatalysts that influence the selection of the reaction pathway is dependent on the electrode potential, i.e., the operating potential of the electrocatalysts themselves.

The operating potential of an electron transfer co-catalyst on a photocatalyst is generally fixed at a certain potential that is intrinsic to the co-catalyst or the semiconductor particles.[16-19] However, for light-energy conversion systems using photoelectrodes, the operating potential of the catalyst changes depending on the balance of the absolute value of the anodic and cathodic currents. Such a modulation of the operating potential might also occur on some sheet-like photocatalysts on which both semiconductor and electron transfer co-catalysts are loaded on a single conductive substrate.^[20-23] The magnitude of the photocurrent is dependent on the light intensity; therefore, in principle, the operating potential of the catalyst could be influenced by the light intensity, as schematically shown in Figure 1a. Thus, for energy-conversion systems with photoelectrodes, fluctuation of the environmental light intensity would lead to a change of the reaction pathway and eventually a change of the reaction products. However, to our best knowledge, there have been no studies that have focused on the light intensity dependence of reaction pathway selection.

In the present work, we attempted to experimentally verify the light intensity dependence of the reaction pathway selection for the light-driven reduction of nitrous acid (HNO₂). Since nitrogen oxides (such as nitrate and HNO₂) contamination due to overfertilization and industrial drainage is becoming a significant issue, the denitrification of wastewater is an urgent need to maintain the global nitrogen cycle. Thus, it is important to understand factors to determine the selectivity of HNO₂ reduction. Here, for HNO₂ photoreduction, we electrically coupled anatase TiO2 with a Cu-modified covalent triazine framework (Cu-CTF)^[24] using two systems: a two-electrodes photoelectrochemical cell without an external bias and a sheet-like photocatalytic device. TiO₂ particles can serve as reaction sites for the photooxidation of methanol, a sacrificial reagent used to provide electrons to the electrical circuit. On the other hand, Cu-CTFs were connected with the circuit as the catalyst for the reduction of HNO2.

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Accordingly, the reduction of HNO₂ on Cu-CTF would, in principle, proceed by coupling with the photooxidation of methanol on TiO₂ via an electrical connection without an external bias, as illustrated in Figure 1b. The reaction products of HNO₂ on the Cu-CTF catalyst are expected to depend on the operating potential^[24-25]; therefore, this reaction system is suitable to verify the light-intensity dependent selection of the reaction pathway.

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Figure 1. Schematic diagrams for (a) the relationship between the operating potential and oxidation/reduction currents, and (b) the photoreduction of nitrous acid via an electrical connection with TiO_2 and Cu-CTF.

Results and Discussion

Model reaction system. Here, we explain the detail of HNO2 reduction on Cu-CTF and why it could be a suitable model system for the present work. In acidic solution,[26-27] HNO2 is spontaneously disproportionated into nitrate (NO3-) and nitric oxide (NO). NO can exist either as surface-bound or soluble species, depending on the adsorption energy of NO. When the adsorption energy is sufficiently weak, the soluble NO is dominant, and the catalyst surface can be free from adsorbates. In this case, HNO₂ can be electrochemically reduced on the catalyst, which results in the direct generation of ammonium ions (NH4⁺) from HNO₂. On the other hand, when the adsorption energy is moderate, reductive dimerization of the surface-bound and soluble NO proceed, which results in the formation of nitrous oxide (N₂O). The adsorption energy of the reaction intermediate is generally dependent on the potential; therefore, the potential also influences the composition of the reaction products. [15, 26-28] The reaction pathway for HNO2 reduction is summarized in Scheme 1. Cu-CTF was selected as the electrocatalyst for HNO₂ reduction for the following reasons. (1) The adsorption energy of NO on Cu-CTF is appropriately moderate $^{\left[24,\ 28-29\right]}\!,$ and (2) the



knowledge obtained through the present work can be generalized

because CTF-based materials can serve as electrocatalysts for

various reactions simply by replacement of the modified metal

species.^[24, 30-38]

Scheme 1. Major reaction pathways for the electrochemical reduction of nitrous acid in acidic electrolytes.

Physical and morphological characterizations of Cu-CTF. Our CTF was obtained through the polymerization of 2,6pyridinedicarbonitrile in the presence of conductive carbon particles (please see the synthesis part) to add electron conductivity. ^[24, 34-38] The resulting CTF was completely insoluble in any common solvents.^[28, 39] Then, the CTF was impregnated in 1 mM CuCl₂ aqueous solutions to dope Cu atoms. Although the detailed characterizations were reported in our previous reports, we again explain those to help readers to understand the detail of our material.^[23-24, 28] The SEM image of a Cu-CTF electrode (Figure 2a) shows the primary particle size of 20-60 nm, corresponding to the size of the added carbon particles. The powder X-ray diffraction (XRD) pattern revealed that our Cu-CTF has an amorphous structure, which is consistent with the reported CTF from 2,6-pyridinedicarbonitrile (Figure S1).[40-41] The atomic concentration of Cu and N atoms were 0.19 and 4.9 %, respectively, which was determined by semi-quantitative X-ray photoelectron spectroscopy (XPS). The narrow N-1s spectra of CTF and Cu-CTF are shown in Figure S2a and S2b, respectively. These spectra could be deconvoluted into C2NH (399.2 eV) and C3N (401.0 eV), as reported by Thomas and coworkers.[42] Notably, the peak assignable to the cyano group in the monomer at 400.5 eV was very small, indicating that the polymerization efficiently proceeded.^[34] The N₂ isotherms and the pore size distribution of Cu-CTF are shown in Figure S3. Cu-CTF has a hierarchical porous structure consisted of micro- and mesopores. The BET surface area was 731 m²/g.

Next, we investigated the Cu atoms in Cu-CTF. Figure 2b shows the Cu-2p XPS spectrum of Cu-CTF. The satellite peaks on the higher binding energy side of the main peak were clearly observed, characterizing the existence of Cu(II).^[43] The Cu-K edge X-ray absorption near edge structure (XANES, Figure 2c) analysis showed that the absorption edge for Cu-CTF located at 8980 eV, which is consistent with that for CuO and Cu(II)-tetraphenylporphyrin (TPP). The XPS and XANES results indicated that the Cu(II) valence state was dominant in Cu-CTF. The coordination environment of the Cu site in Cu-CTF was investigated by the extended X-ray absorption fine structure (EXAFS, Figure 2d). The Cu-N peak at 0.16 nm was clearly

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observed, whereas the peaks assignable to Cu-Cu peak (0.22 nm) or Cu-O-Cu (0.27 nm) were not detected.^[28] Therefore, the Cu atoms in Cu-CTF were almost atomically dispersed. The peak intensity of Cu-N for Cu-CTF was lower than that for Cu-TPP, suggesting that the coordination number of N atoms in Cu-CTF is smaller than 4. In fact, the coordination number had been calculated to be 3.4 based on the EXAFS fitting, as reported in our previous manuscript.^[24] This unsaturated coordination structure of Cu sites leads to the strong adsorption of adsorbate because of a low steric hindrance and more accessible d-orbitals.^[29] In the case of nitrogen oxides reduction reactions, the Cu site in Cu-CTF strongly binds and effectively reduces NO, as mentioned above and in our previous works.^[23-24]



Figure 2. (a) The representative SEM image of a Cu-CTF electrode. Scale bar: 200 nm. (b) Cu-2p XPS spectrum of Cu-CTF (c) The Cu-K XANES spectra for Cu (gray), Cu₂O (green), CuO (brown), Cu(II)-TPP (blue) and Cu-CTF (red). (d) k^3 -weighted FT-EXAFS spectra of the Cu-K edge for Cu-CTF (red), Cu(II)-TPP (blue), and Cu metal (gray).

Half-cell electrochemical measurements. Current density (i) vs. potential (U) curves for the TiO₂ electrode are shown in Figure 3a, in which 0.1 M methanol was added as a sacrificial reagent to generate photoexcited electrons for other reactions. The onset potential of the anodic photocurrent was -0.34 V, which corresponds to the flat band potential of anatase TiO₂. The j vs. U curves obtained for the Cu-CTF on FTO in a perchloric acid (HClO₄) electrolyte with (blue curve) and without (black curve) dissolved HNO₂ are also shown in Figure 3a. A comparison of the two curves in this figure reveals that the onset potential for the reduction current on Cu-CTF located at +0.05 V vs. Ag/AgCl. We also performed chronoamperometry at -0.3 V vs. Ag/AgCl with and without HNO₂ (Figure S4). The cathodic current largely increased on Cu-CTF by the addition of HNO₂ at -0.3 V. Thus, the onset potential of the photoelectrochemical oxidation of methanol on TiO₂ (-0.34 V) was more negative than that of HNO₂ reduction on Cu-CTF, which indicates that HNO2 reduction can spontaneously proceed when coupled with the photooxidation

reaction on TiO_2 without an external bias, which will be verified later.

DEMS analyses were performed simultaneously with voltammetry measurements in 0.1 M HClO₄ containing 0.1 M methanol (Figure 3b). The onset potentials for the increase of the $^{15}N_2O$ signal (m/z = 46) and the cathodic current correlated well with each other, which indicates that the reductive dimerization of NO is the dominant process in this potential region. Although the ¹⁵N₂O signal initially increased with the negative potential shift, the signal began to decrease after exhibiting a peak at around -0.05 V. The cathodic current then continued to increase, even after ¹⁵N₂O began to decrease, which indicates that the contribution of the reductive dimerization reaction to the total reduction current gradually decreases, and other reactions become dominant with the negative potential shift. Thus, the reaction mechanisms (i.e., the reaction pathway) for HNO₂ reduction change depending on the potential. To clarify the dominant reaction pathway in the negative potential region, the reaction products were analyzed using chromatography. NH₄⁺ was the main products (Figure 3c), which suggests that HNO₂ can be directly reduced on Cu-CTF in this potential region.

The reaction pathway for HNO₂ reduction can be summarized as follows. First, HNO₂ is partially disproportionated to NO and NO₃. Under positive potentials, the surface-bound NO and soluble NO are then reductively dimerized to form N₂O. On the other hand, under negative potentials, HNO₂ can be directly reduced on Cu-CTF, which leads to the generation of NH₄⁺. It was confirmed that the onset potential of the NO₃⁻ reduction current - 0.70 V (Figure S5), which was out of the potential region of interest in this study.^[23-24] The complete results described here are essentially consistent with that shown in Scheme 1. However, it should be noted that the reaction pathway is changed according to the potential of Cu-CTF.



Figure 3. (a) Polarization curves obtained with (upper) TiO₂ and (lower) Cu-CTF acquired at a scan rate of 10 mV s⁻¹. Electrolyte: (upper) 0.1 M HClO₄ containing 0.1 M methanol at a light intensity of 1 mW cm⁻² (red), and (downer) 0.1 M HClO₄ containing 0.1 M methanol with/without 10 mM HNO₂. (b) Mass signals assigned to ¹⁵N₂O and the corresponding currents on Cu-CTF in 0.1 M HClO₄ containing

0.1 M methanol with 10 mM HNO₂. (c) Faradaic efficiency during the HNO₂ reduction reaction using Cu-CTF in 0.1 M HClO₄ containing 0.1 M methanol with 10 mM HNO₂ at -0.4 V.

Light-intensity dependent selection of the reaction pathway.

Here, we evaluate the photo-driven nitrous acid reduction activity of the couple of TiO₂/Cu-CTF by fabricating a sheet-like photocatalytic device and a two-electrodes electrochemical cell. The sheet-like photocatalytic device incorporating both Cu-CTF and TiO₂ were prepared on a single FTO (Figure S6). As shown in Figure 3a, the onset potential for the photooxidation current on TiO₂ was more negative than that for the cathodic HNO₂ reduction current on Cu-CTF. Therefore, HNO₂ reduction on the devices is expected to occur spontaneously based on the principle of local cell reactions under irradiation conditions.[23, 44] The device was irradiated with UV light (350-400 nm) at light intensities of 0.6, 2, and 20 mW cm⁻². The generation of N₂O was confirmed to increase with time by in situ mass analysis (Figure 4a), which clearly indicates that the photo-driven reduction of N₂O proceeded on the device. Although the operating potential was monotonically shifted to the negative side with an increase in the light intensity. the generation of N₂O decreased under the highest light intensity (20 mW/cm⁻²). Considering that the operating potential of this device was about -0.3 V at 20 mW/cm⁻², this result is well consistent with the relationship between the potential and the N_2O generation rate that was obtained by DEMS measurements (Figure 3b).

The product distribution depending on light intensity was investigated a double-chamber electrochemical cell in which the two chambers were separated by a Nafion membrane (Figure S7) to focus on only HNO₂ reduction reaction at Cu-CTF. It is noted here that this cell was operated in a short-circuit condition in a similar manner to the sheet-like photocatalysts on a single conductive substrate. The ratio and amounts of reaction products after 6 h of light irradiation are summarized in Figure 4b and Table S1a, respectively. The major products were N₂O and NH₄⁺, which were detected by using gas chromatography mass spectrometry (GCMS, Figure S8) and ion chromatography, respectively. The amounts of other products, such as N2 and hydroxylammonium ions were almost below the detection limit. The time courses of the device potential during light irradiation are also shown in Figure 4c. At a light intensity of 1 mW cm⁻², N₂O was the dominant product, and a small amount of NH4⁺ was detected (ca. 10 %). When increasing the light intensity to 9 mW cm⁻², the ratio of NH₄+ drastically increased to over 40 %. The external quantum efficiency (QEs) for each product are summarized in Table S1b (for the calculation detail, see Supporting Information). When changing the light intensity from 1 mW cm⁻² to 9 mW cm⁻², the QE of N₂O decreased from 5% to 1%. Notably, the XANES spectrum of Cu-CTF did not at all change after the catalyst test under 1 mW cm⁻², indicating that our catalysts are stable in these reaction conditions (Figure S9). Although the reason why the potential gradually shifted to the negative side during the photoreaction is still unclear (Figure 4c), the decrease in HNO₂ substate might cause the lower cathodic current and the negative shift of the operating potential. We would like to discuss this issue as future work quantitatively.

Notably, the anodic photocurrent of TiO_2 with and without HNO_2 was also measured using the half-cell setup to confirm if HNO_2 reduction proceeded directly on TiO_2 (Figure S10). The

onset potential of the anodic photocurrent was not influenced by the addition of HNO_2 , which indicates that the electrons excited on TiO_2 were not transferred to HNO_2 but to the FTO electrodes, despite the presence of HNO_2 . Therefore, the reduction of HNO_2 occurred only on Cu-CTF in this device.



Figure 4. (a) Nitrous acid reduction yield 6 h after initiation of the reaction in 0.1 M HClO₄ containing 0.1 M methanol with 10 mM HNO₂. (b) Time course of the operating potential at light intensities of 1 mW cm⁻² (red), and 9 mW cm⁻² (blue). (c) Changes in operating potential (blue) and mass signals assigned to ¹⁵N₂O (m/z=46) generated by HNO₂ reduction on Cu-CTF (red) with changes in the light intensity. Electrolyte: 0.1 M HClO₄ containing 0.1 M methanol with 10 mM HNO₂.

Reaction selectivity under naturally fluctuating sunlight. The intensity of natural sunlight fluctuates dynamically due to the Earth's rotation and changes in the weather. In view of the above conclusion, the composition of the reaction products would thus fluctuate under irradiation with natural sunlight. This was verified by quantifying the amounts of reaction products obtained under natural sunlight using the same double-chamber electrochemical cell (Figure 5a). The area of TiO₂ coated FTO (36 cm²) for this experiment was larger than that used under artificial light (2 cm²) (for the detail, see experimental section). Figure 5b shows the amount of N₂O generated every 2 h. N₂O generation decreased at the third period (12:30-14:30) compared with that at the second period (10:00-12:00), although the intensity of sunlight increased (Figures 5b and c). Considering the measured operating potential, this result is consistent with the results using artificial light. In addition, Figure S11 shows this relationship among N₂O production, sunlight intensity, and operating potentials obtained on other days. These results indicate that the light-energy conversion systems used under natural sunlight should be designed with consideration of the dynamic change in the catalyst operating potential.



Figure 5. (a) Photograph and schematic diagram of the reactor. (b) Amount of N_2O generated every 2 h. (c) Time course of the operating potential (red) and sunlight intensity (black) under natural sunlight. Date and place: 16/10/2019 in Toyonaka, Osaka, Japan.

Conclusion

The reaction pathway for photo-driven HNO₂ reduction on substrates with TiO₂ and Cu-CTF was demonstrated to be dependent on the light intensity. The potential of the device was determined by the balance of the absolute photooxidation and reduction currents. Therefore, when the light intensity is increased (or decreased), the balanced potential shifts negatively (or positively). According to the shift of the potential, the reaction pathway is altered, which results in a change of the composition of the reaction products. This study has thus shown experimentally that it is necessary to consider the light-intensity dependent change of the catalyst potential when constructing light-energy conversion systems with photoelectrodes. This is especially important for systems where multiple products can be generated under fluctuating light intensity, such as the solar-driven reduction of carbon dioxide and nitrogen oxides.

We must note that the operating potential in this system is limited by a conduction band bottom of n-type semiconductors (e.g., -0.3 V vs. RHE for anatase TiO₂). Considering that the operating potential for CO₂ reduction is generally more negative than -0.6 V vs. RHE, TiO₂ cannot be utilized for the CO₂ reduction reaction. Recently, several n-type semiconductors with more negative conduction band bottoms, such as TaON, Ta₂O₅ and g-C₃N₄, have been reported as photocatalysts for CO₂ reduction.^[1, 45-48] These n-type semiconductors can also oxidize water to O₂ in the presence of appropriate co-catalysts. When we utilize these semiconductors for CO₂ reduction reactions, the insight provided by this work will become quite important.

Experimental Section

Synthesis of Cu-CTFs. CTF was prepared by the same method as described in our previous reports.^[23-24] Briefly, 2,6-pyridinedicarbonitrile (64.5 mg, Aldrich) and KetjenBlack (64.5 mg, EC600JD, Lion Corp.) were mixed with ZnCl₂ (6.82 g, Wako) in a vacuum glass tube, and then heated at 400 °C for 40 h. After cooling down to room temperature, the resultant power was washed with deionized water, tetrahydrofuran (THF), and HCl (1 M, Wako), and was then modified with Cu atoms by stirring for 2 h at 60 °C in 1 mM CuCl₂ aqueous solution. The products were subsequently collected by centrifugation and washed thoroughly with deionized water to remove residual metal salt.

Electrode Preparation and Characterization. The Cu-CTF electrode was fabricated as follows. 5 mg Cu-CTF catalyst and 100 μ L Nafion (5 wt%, Du Pont, Corp.) were homogeneously dispersed in 200 μ L ethanol. 50 μ L of the obtained catalyst ink was dropped onto a glassy carbon plate (2 cm²), and was then left to dry in air at room temperature to yield a catalyst layer with a loading weight of 0.4 mg cm⁻². For *in situ* differential electrochemical mass spectrometry (DEMS) measurements, 30 μ L of catalyst ink was dropped onto a glassy carbon electrode (0.07 cm⁻²).^[49]

The TiO₂ electrode was prepared according to the reported protocol.^[50] TiO₂ powder (3.2 g, anatase form, surface area 52 m² g⁻¹; AMT-600, TAYCA) was homogeneously dispersed into a solution of distilled water (35.2 mL), acetyl-acetone (0.64 mL), nitric acid (60%, 0.8 mL), and polyoxyethylene-p-isooctylphenol (0.835 mL, Triton X-100). The solution was applied onto a fluorine-doped tin oxide (FTO) substrate (resistance of ca. 7 Ω sq⁻¹, Aldrich) using a spin-coater at 2000 rpm, which was heated at 150 °C. This was repeated four times and was followed by calcination at 500 °C for 3 h.

XPS spectra were measured using monochromatic AI K α Xrays at hv = 1486.6 eV. X-ray absorption fine structure (XAFS) measurements were performed using the hard X-ray BL01B01 beamline at SPring-8, Japan. SEM was performed on a field emission scanning electron microscope (FE-SEM; S-5000, Hitachi). A powder XRD pattern was obtained using a PANalytical X'Pert PRO diffractometer with Cu K α radiation. The N₂ isotherm was recorded by a Micromeritics 3 Flex at 77 K.

Half-cell electrochemical measurements. Electrochemical measurements were undertaken using an electrochemical station (HZ-5000, Hokuto Denko). A Ag/AgCl (saturated KCl as inner solution) electrode and the titanium wire were used as reference and counter electrodes, respectively. HNO₂ reduction activities were measured in 0.1 M HClO₄ solutions (pH 1) containing 0.1 M methanol. ¹⁵N-labeled sodium nitrite (Cambridge Isotope Laboratories) was used as a HNO₂ source to exclude the possibility of detecting products from the degradation of the CTF. Details of the *in situ* DEMS analysis are described in the previous study. ^[49] DEMS signals of 30 (fragment of ¹⁵N₂O and ¹⁵N₂), 31 (¹⁵NO and fragment of ¹⁵N₂O), and 46 (¹⁵N₂O) were recorded.

Photocatalytic test by the sheet-like devices incorporating both Cu-CTF and TiO₂. After preparing the TiO₂ layer on half the area of the FTO substrate (4 x 5 cm), a graphite sheet (1 x 1 cm ×17 μ m, EYGS091202, Panasonic,) was pasted next to the TiO₂

layer using conductive silver paste (Dotite) and epoxy resin. 15 μ L of Cu-CTF catalyst ink was dropped on the paper and left to dry at room temperature to obtain a photocatalytic device (Figure S6). The reaction was started by UV light irradiation (Lightningcure UV-LED LC-LIVB, Hamamatsu, 350–400 nm). A Ag/AgCl (saturated KCl as inner solution) was used as a reference electrode. The *in situ* mass analysis was conducted using the same setup with DEMS.

Photocatalytic test by using the double-chamber electrochemical cell. A double-chamber electrochemical cell with a Nafion membrane was used to evaluate product distribution. The cell used under artificial and natural light is shown in Figure S7. The accumulated gaseous products were analyzed using gas chromatography mass spectrometry (GCMS; GCMS-QP 2010 Plus, Shimadzu, Japan), while the ammonia and hydroxylamine concentrations were determined using ion chromatography (Prominence HIC-SP, Shimadzu, Japan). The area of TiO₂ anode was 2 cm² and 36 cm² under artificial and natural light, respectively.

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The Cu-doped covalent triazine framework/TiO₂ hybrid photocatalytically reduced HNO_2 without an external bias under artificial light and natural sunlight. The dominant reaction product changes from N₂O to NH_4^+ with an increase in the light intensity due to the shift of operating potentials.