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Photocatalytic evolution of nitrous oxide from nitric monoxide over Pt-loaded titanium dioxide under UV irradiation†

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This study presents a photocatalytic evolution of nitrous oxide (N$_2$O) from nitric monoxide (NO), well known as a harmful gas contained in exhaust gas. Pt nanoparticles (NPs) were loaded on titanium dioxide (TiO$_2$) using different methods including impregnation, photo-deposition and chemical reduction methods. Bare TiO$_2$ (without metal loading) did not exhibit high N$_2$O evolution under UV irradiation, but all Pt-loaded TiO$_2$ photocatalysts did exhibit improved N$_2$O evolution.

Despite nitrous oxide (N$_2$O) being the "third" greenhouse gas, it has recently attracted attention in various fields. In the petrochemical industry, selective oxidation of hydrocarbons is vital for producing valuable fine chemicals,[1] and there has been growing interest in utilizing green and atom-efficient oxidants such as H$_2$O$_2$ and N$_2$O for catalytic oxidation.[2] Both H$_2$O$_2$ and N$_2$O release monoatomic oxygen, forming harmless H$_2$O and N$_2$, respectively. N$_2$O, in particular, is suitable as an oxidant in liquid and gas-phase reactions due to its high solubility in nonpolar media and gaseous nature. For instance, catalytic oxidation of CH$_4$ into methanol using N$_2$O over zeolites has been proposed, converting two greenhouse gases into a useful chemical.[3,4] In the medical field, the demand of N$_2$O, also known as "laughing gas," has been increasing.[5,6] Considering these advantages, N$_2$O holds significant potential for clean technologies in fine chemical synthesis and medical developments.

Plant-scale manufacturing of N$_2$O was done at Jinhong Gas and Heng'an Gas Co., Ltd., where the decomposition of NH$_4$-

NO$_3$ is used for N$_2$O production. According to interviews with these companies, N$_2$O produced through the current process is available to only high-end users in practical applications because of the high cost of the process (approximately 3000–5000 \$ per Mg).[7] The oxidation of NH$_3$ is considered an alternative reaction for N$_2$O production.[7,8] However, there are concerns about the current price increase of NH$_3$, which is probably a barrier to achieving inexpensive N$_2$O production. As is well known, anthropogenic N$_2$O is mainly released into the atmosphere during agricultural and industrial activities,[9] and N$_2$O capture can be a promising technique for the effective utilization of N$_2$O.[10,11] However, the concentration of N$_2$O in the atmosphere is quite low (approximately 0.3–0.4 ppm). Many types of gas molecules, such as CO$_2$ and H$_2$O, are also present in the atmosphere, which makes selective separation of N$_2$O in the atmosphere further challenging. Considering the future demand of N$_2$O, further implementation of low-cost N$_2$O production is highly recommended.

Nitric monoxide (NO) is a well-known gaseous pollutant that mainly comes from the exhaust gases of automobiles, plants, and thermal power stations. In current de-NOx systems, NO is converted into N$_2$ through selective catalytic reduction with NH$_3$ over zeolites[12,13] or V-based TiO$_2$[14,15] before being discharged into the atmosphere. Recently, the use of NO as a feed gas for valuable nitrogen compounds has been a focus of research. For example, in several studies, the catalytic conversion of NO to NH$_3$ has been investigated.[16–20] Thus, NO has great potential as a feed gas toward the low-cost production of N$_2$O.

Here, the photocatalytic evolution of N$_2$O from NO as the feed gas over Pt-loaded TiO$_2$ is reported. Pt NPs were loaded onto TiO$_2$ (P25) using different loading methods. The photocatalysts hardly converted NO into N$_2$O without ultraviolet (UV) irradiation, and the amount of N$_2$O evolved increased under UV irradiation. Additionally, the Pt-loaded TiO$_2$ photocatalyst exhibited higher N$_2$O evolution than did the bare TiO$_2$ photocatalyst, suggesting that Pt species can act as active sites in this case. These findings should help

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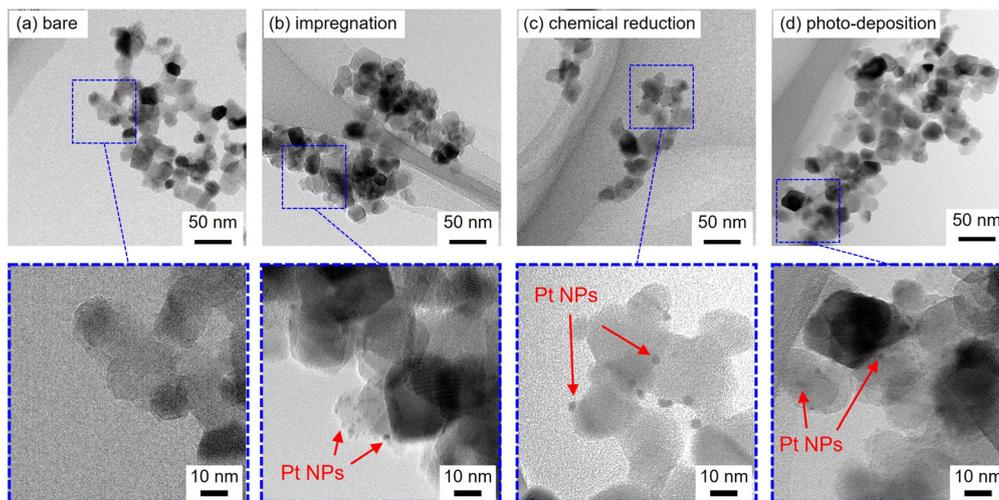**Fig. 1** TEM images of (a) bare and (b–d) Pt-loaded TiO$_2$ photocatalysts prepared using different loading methods, namely (b) impregnation, (c) chemical reduction and (d) photo-deposition.

promote the development of N$_2$O production from a low-cost feedstock.

Pt-loaded TiO$_2$ photocatalysts were synthesized using different loading methods, including chemical reduction, impregnation, and photo-deposition methods, and are denoted as Pt/TiO$_2$-cr, Pt/TiO$_2$-imp and Pt/TiO$_2$-pd, respectively. The details of the syntheses and characterizations of the photocatalysts are described in the ESI.† Fig. 1 shows transmission electron microscopy (TEM) images of the bare and Pt-loaded TiO$_2$ photocatalysts. Bare P25 was composed of small TiO$_2$ NPs with diameters of less than 20 nm, as shown in Fig. 1(a). Spherical Pt NPs were located on the surface of the TiO$_2$ NPs, and the Pt particles were less than 10 nm in diameter, as shown in Fig. 1(b–d). X-ray diffraction confirmed that the crystalline phase and the crystalline sizes of TiO$_2$ were not affected by Pt loading (Fig. S1, Table S1†). All of the Pt-loaded TiO$_2$ samples became black in color upon being loaded with Pt,

and UV-vis spectra of the Pt-loaded TiO$_2$ indicated light absorption in the visible-light region, due to the surface plasmon resonance of Pt NPs (Fig. S2†). The characteristics of the Pt NPs in the Pt-loaded TiO$_2$ photocatalysts are summarized in Table S1.† TEM images indicated that the particle sizes of Pt followed in the order Pt/TiO$_2$-cr > Pt/TiO$_2$-pd > Pt/TiO$_2$-imp. Dispersion of Pt determined from CO pulse measurements followed in the order Pt/TiO$_2$-imp > Pt/TiO$_2$-pd > Pt/TiO$_2$-cr. These results confirmed that the accessible surface area of the Pt NPs followed in the order Pt/TiO$_2$-imp > Pt/TiO$_2$-pd > Pt/TiO$_2$-cr. X-ray fluorescence revealed that there was no significant difference in Pt content among the three photocatalysts (1.7–1.8 wt%). Therefore, the three Pt-loaded TiO$_2$ photocatalysts with almost the same amount of Pt NPs and with different particle sizes were obtained.

Photocatalytic conversions of NO into N$_2$O over Pt-loaded TiO$_2$ photocatalysts were investigated using a quartz fixed-
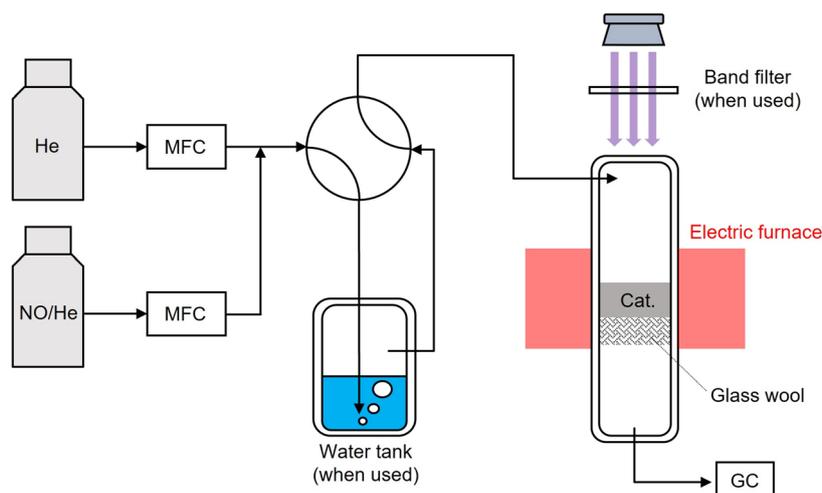

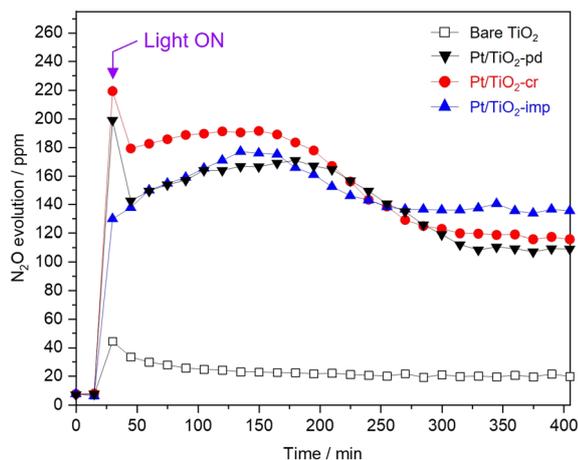**Fig. 2** Schematic of the fixed-bed reactor made in house.

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Fig. 3 N$_2$O evolutions over different photocatalysts. Photocatalytic tests were carried out at an SV of 3500 h^{-1}.

bed reactor made in house (Fig. 2). Typically, the input gas was passed through the water tank, and UV light was irradiated onto the upper side of the photocatalysts. Prior to photocatalytic tests, samples were pre-treated to completely rid them of carbon species. The details for the photocatalytic tests are described in ESI.† N$_2$O evolutions over different photocatalysts were compared in Fig. 3. None of the photocatalysts without UV irradiation produced any considerable amount of N$_2$O. Upon UV irradiation, the evolved amount of N$_2$O over bare TiO$_2$ increased to some extent, and considerably more so did (>100 ppm) over each of the three Pt-loaded TiO$_2$ photocatalysts. These results were indicative of N$_2$O evolution having been accelerated by light irradiation and of Pt NPs playing a key role in enhancing N$_2$O evolution. Reaction mechanism is hereafter discussed using Pt/TiO$_2$-pd as the photocatalyst.

Fig. 4 shows representative gas chromatography (GC) profiles of the outlet gases in the photocatalytic tests under UV irradiation. No considerable peak was observed under He flow (in the absence of NO). When NO/He was introduced as
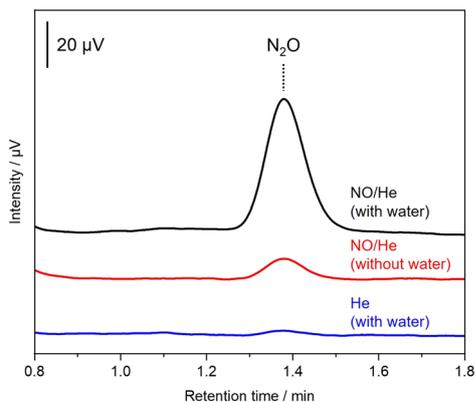
the feedstock gas, there was a peak at 1.36 min, which could be assigned to N$_2$O. This result indicated that N$_2$O evolved from the introduced NO. A decreased N$_2$O evolution was observed when water was not introduced into the reaction system, suggestive of water also playing a part in the photocatalytic reaction.

Fig. 5 shows GC profiles in the region of 6.5–7.5 min at various gas hourly space velocity (GHSV) values. No peak was observed at 7 min for a GHSV of 3500 h^{-1} (black line), but peaks at 7 min became obvious at lower GHSV values (red and blue lines). These peaks can be assigned to O$_2$. Furthermore, the peaks originating from O$_2$ evolution were not observed at 7 min without UV irradiation (dashed, blue line). In summary, O$_2$ evolution was found to be triggered by UV irradiation together with N$_2$O evolution from NO feed stock. Fig. 6 shows a schematic illustration explaining the proposed mechanism for photocatalytic evolution of N$_2$O over TiO$_2$ with Pt loading. The reductive/oxidative and overall reactions of this system were estimated, and each potential *versus* a normal hydrogen electrode (NHE) can be presented as follows.

Reductive reaction:

$$4NO + 4H^+ + 4e^- \rightarrow 2N_2O + 2H_2O \quad (1.54 \text{ V } vs. \text{ NHE}) \quad (1)$$

Fig. 5 GC profiles of the product gas over Pt/TiO$_2$-pd under UV irradiation at different SV conditions.

Fig. 4 GC profiles of the gases produced from different feed stocks. The catalytic tests were carried out using Pt/TiO$_2$-pd under UV irradiation at an SV of 3500 h^{-1}.
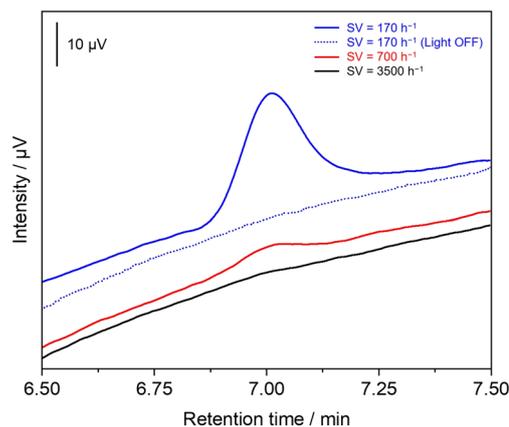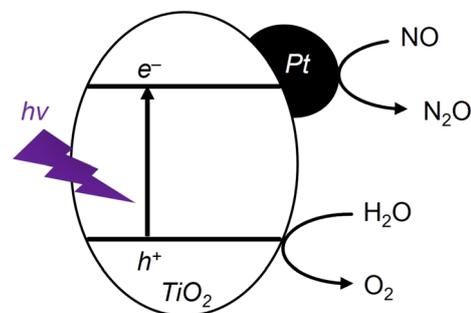

Fig. 6 Proposed mechanism for N$_2$O evolution over Pt-loaded TiO$_2$ under UV irradiation.

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Oxidative reaction:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (1.23 \text{ V } vs. \text{ NHE}) \quad (2)$$

Overall reaction:

$$4NO \rightarrow 2N_2O + O_2 \quad (3)$$
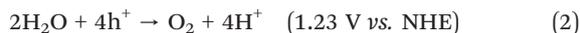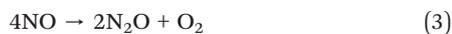
Considering the band positions of TiO_2 (conduction band: −0.38 V *vs.* NHE, valence band: 2.82 V *vs.* NHE),[21,22] this photocatalytic reaction (eqn (1) and (2)) would be expected to be able to proceed. Furthermore, consideration of the calculated equilibrium conversion rate (Fig. S3†) suggested the overall reaction (eqn (3)) to be thermodynamically accessible. As for O_2 in this reaction, inspection of the stoichiometry of eqn (3) would suggest an evolution of half as much O_2 as N_2O by molarity, but the measured amount of evolved O_2 was considerably lower (Fig. S4†). Nitrogen dioxide (NO_2) was detected in the outlet gas by using a Fourier transform infrared detector, suggesting that some of the O_2 reacted with unreacted NO to form (NO_2) as shown in eqn (4).

$$2NO + O_2 \rightarrow 2NO_2 \quad (4)$$

As shown in Fig. 3, Pt loading was observed to enhance the photocatalytic evolution of N_2O, attributed to efficient separation of photogenerated charges. The apparent quantum yield (AQY) was calculated to be 4.4%. This value was comparably higher in gas-phase photocatalysis. Previous research showed the hygroscopic nature of the metal oxide having dramatically increased the AQY of photocatalytic water splitting.[23,24] In the currently investigated N_2O evolution reaction, Pt-loaded TiO_2 seemed to be quite hygroscopic, resulting in high AQY.

In summary, low-cost N_2O manufacturing approach using NO as feed was proposed. The photocatalysts tested hardly converted NO into N_2O without UV irradiation, and the amount of N_2O that evolved increased under UV irradiation. In particular, the Pt-loaded TiO_2 photocatalyst exhibited higher N_2O evolution than did the bare TiO_2 photocatalyst, suggesting that Pt enhanced the efficiency of photogenerated charges. Furthermore, decreased evolution of N_2O was observed without H_2O, indicative of the involvement of H_2O in this photocatalytic reaction. To the best of our knowledge, this was the first study to demonstrate the photocatalytic evolution of N_2O from NO. Although further improvements (*e.g.*, suppression of oxidation of NO and increase of conversion rate) is still required, these findings should be considered to help promote the development of N_2O production from a low-cost feedstock.

Data availability

The data that support the findings of this study are openly available.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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