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► **To cite this version:**

Oriane Delaunay, Eya Zghab, Audrey Denicourt-Nowicki, Alain Roucoux. Photocatalytic Oxygen Transfer as an Innovative Route for N<sub>2</sub>O Upgrading. *ChemCatChem*, 2023, 15 (6), 10.1002/cctc.202201517 . hal-04007732

**HAL Id: hal-04007732**

**<https://hal.science/hal-04007732v1>**

Submitted on 28 Feb 2023

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# Photocatalytic oxygen transfer as an innovative route for N<sub>2</sub>O upgrading

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**Abstract:** As concentration of nitrous oxide (N<sub>2</sub>O) keeps growing steeply in the atmosphere, upgrading this anthropogenic greenhouse gas as a potential oxygen transfer agent constitutes a real challenge to limit global warming and ozone layer depletion. Decomposition of N<sub>2</sub>O is mainly described under highly energy-consuming thermal activation, owing to its high stability and large activation barrier, making it kinetically inert. Herein, we demonstrate the controlled photocatalytic upgrading of N<sub>2</sub>O as an oxygen atom donor, releasing only dinitrogen (N<sub>2</sub>) as a benign co-product. The doped Ag@TiO<sub>2</sub> photocatalyst specifically activates N<sub>2</sub>O for controlled oxidation of phosphines avoiding mineralization, under mild conditions (room temperature, 1 atm,  $\lambda = 365$  nm), as a proof-of-concept of the valorization of N<sub>2</sub>O as an oxygen transfer agent. The catalytic system is active and selective in various organic solvents, as well as innovatively in water, depending on the phosphine structure.

**Keywords:** nitrous oxide, oxygen transfer, photocatalysis, sustainable chemistry, silver on titanium dioxide.

## Introduction

Nitrous oxide (N<sub>2</sub>O), also known as “laughing gas”, is the third greenhouse effect gas (GEG) emitted in the atmosphere by anthropogenic activities (agriculture, biomass burning, nitric acid and adipic acid production, etc.) after carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). In the coming years, this gas, which has steeply increased over the recent decades, will be controlled by drastic international regulation owing to its global warming effect (almost 300 times more powerful than CO<sub>2</sub>) and its atmospheric lifetime of *ca.* 110 years.<sup>1</sup> Industries generating this waste, such as in the production of adipic acid, currently burn this gas in flares,<sup>2</sup> but in the drive towards more sustainable chemical processes, this GEG could be upgraded as an oxygen source to produce marketable chemicals, only generating dinitrogen (N<sub>2</sub>) as a benign co-product.

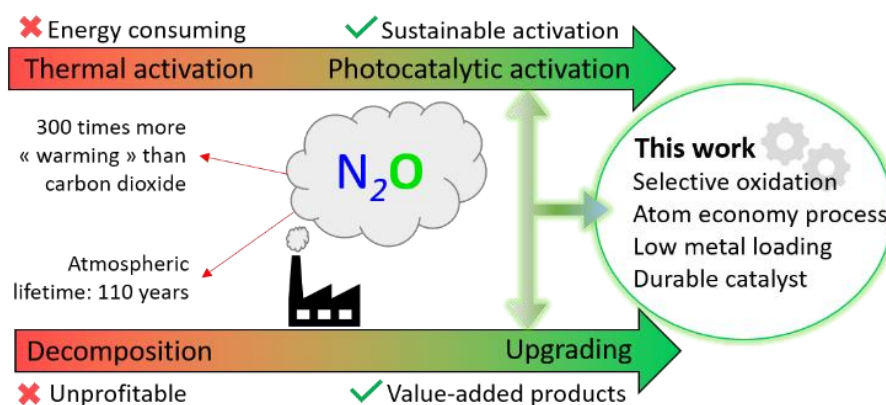
Kinetically recalcitrant toward decomposition and reduction,<sup>3</sup> this gas is generally decomposed through catalytic activation at temperature above 400 °C with heterogeneous catalysts to provide

oxygen and nitrogen,<sup>4</sup> sometimes with the combined use of simple reducing additives like methane,<sup>5-7</sup> carbon monoxide,<sup>4</sup> propane<sup>8</sup> or benzene.<sup>9,10</sup> A few homogeneous catalysts (ruthenium, rhenium, or rhodium complexes) have also been described for nitrous oxide reduction into nitrogen under moderated temperatures (rt to 50 °C).<sup>11,12</sup>

While targeting oxidation reactions under N<sub>2</sub>O atmosphere, phosphines can interestingly be used as “probes” to demonstrate the oxygen transfer to the phosphorus atom. This novel approach can be an eco-responsible alternative to the traditional production of phosphines oxides in presence of oxygen or peroxides, with poor selectivity control and generation of chemical waste.<sup>13</sup> Uncommon cobalt, ruthenium or nickel complexes have already been applied for phosphines oxidation under N<sub>2</sub>O atmosphere.<sup>13-16</sup> Nevertheless, no correlation with N<sub>2</sub> production has been demonstrated providing an oxygen source ambiguity, and the designed complexes require high loading (≈20 % mol) to activate N<sub>2</sub>O and are often more sensitive than robust heterogeneous catalysts.

Photocatalysis for chemical synthesis has gained interest as a sustainable alternative to more energy-consuming processes. Thus, oxidation reactions are performed under mild conditions (UV-Visible light, room temperature, and atmospheric pressure of O<sub>2</sub>) with a semiconductor matrix such as TiO<sub>2</sub>, ZnO or CdS, that can be recycled and potentially reused.<sup>17</sup> The key challenge remains the efficient selectivity control to avoid over-oxidation and mineralization of the organic compounds into carbon dioxide and water.

Catalysts based on zeolites<sup>18-22</sup> or titanium dioxide<sup>23-25</sup> supports have been described for N<sub>2</sub>O photodecomposition with different metals as active species (copper,<sup>18, 19, 25</sup> lead,<sup>20</sup> silver,<sup>21, 24-26</sup> titanium,<sup>22</sup> cerium<sup>23</sup>), without<sup>18, 19, 21, 23, 24</sup> or with a sacrificial reducing agent for N<sub>2</sub>O (propane,<sup>20</sup> carbon monoxide<sup>22</sup> or methanol<sup>25, 26</sup>). Nevertheless, no direct strategy describes selective photooxidation of an organic compound in solution by oxygen transfer from N<sub>2</sub>O, thus upgrading this industrial waste as a clean oxygen donor to produce high value-added compounds (Figure 1).

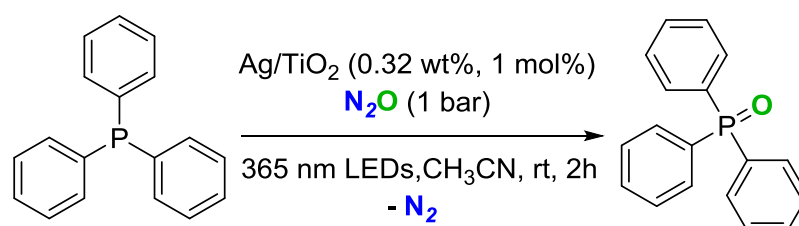


**Figure 1.** Upgrading nitrous oxide for controlled oxidation reactions.

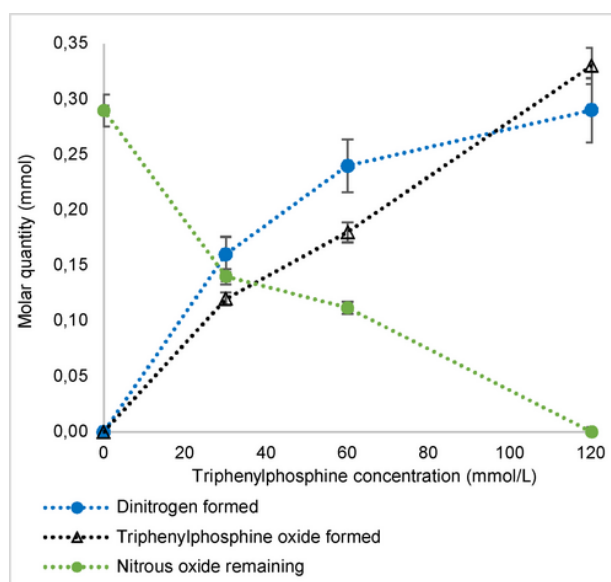
Herein, we describe an oxygen transfer from  $N_2O$  to phosphines under photocatalytic activation in a gas-liquid-solid system as an innovative way to upgrade this gas waste.

## Results and Discussion

Silver deposited on titanium dioxide ( $Ag/TiO_2$ ) catalyst was selected given its high activity in photocatalytic processes, and its easy preparation method by photodeposition.<sup>26</sup> To unlock the use of  $N_2O$  as a potential oxygen atom transfer, triphenylphosphine ( $PPh_3$ ) was used as an “oxygen probe” (Scheme 1).



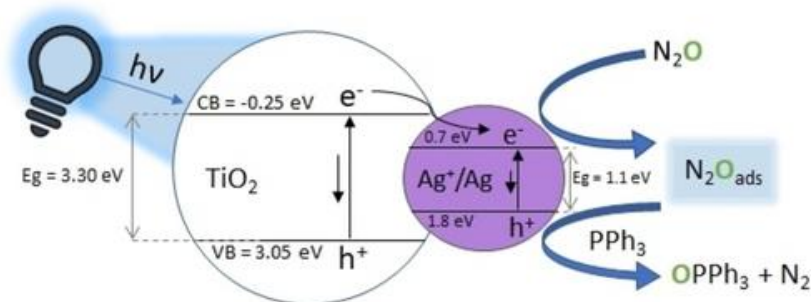
**Scheme 1.**  $Ag/TiO_2$  catalyzed photocatalytic activation of  $N_2O$  coupled with oxidation of triphenylphosphine. The oxygen atom transfer from  $N_2O$  to  $PPh_3$  was observed with a 99% yield, with release of dinitrogen as sole benign co-product. Figure 2 shows the good correlation between the amount of  $N_2O$  consumed overnight and the quantities of  $N_2$  and triphenylphosphine oxide formed, thus demonstrating the role of  $N_2O$  as unique and selective oxygen-donor under light activation of the doped  $Ag-TiO_2$  photocatalyst.



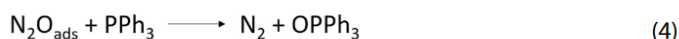
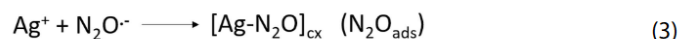
**Figure 2.** Evolution of  $N_2O$  amount,  $N_2$  and triphenylphosphine oxide formed during the reaction vs triphenylphosphine concentration after complete conversion. Reaction conditions: catalyst  $Ag/TiO_2$  (0.32 wt %  $Ag$ ), triphenylphosphine (0.09–0.36 mmol), substrate/silver molar ratio=100, 1 bar of pure  $N_2O$  (0.29 mmol in

gas phase, 7 mL), 3 mL of CH<sub>3</sub>CN, 365 nm irradiation (two LEDs, 150 mW/cm<sup>2</sup>), overnight, room temperature. Triphenylphosphine oxide quantified by GC-FID with 1,2-dichlorobenzene as external standard (Figure S8). Gas phase quantified by GC-BID detector (Figure S6 & S7).

A mechanism for oxygen transfer from N<sub>2</sub>O to phosphines with Ag/TiO<sub>2</sub> excited under UV light is proposed in Scheme 2. To argue it, preliminary blank tests were performed to validate the photocatalytic system and mechanism and exclude artefacts in results (Table S4). First, no conversion was observed in the absence of N<sub>2</sub>O (under an argon atmosphere), as well as without catalyst. The light irradiation at 365 nm (maximum absorbance of TiO<sub>2</sub>) was essential to activate the photocatalyst and produce positive holes (h<sup>+</sup>) as well as electrons (e<sup>-</sup>) [Equation (1)] that promote N<sub>2</sub>O reduction.<sup>27, 28</sup> Its crucial role was assumed by a switch on-switch off experiment (Figure S9). UV analyses performed on the catalyst showed that doping TiO<sub>2</sub> with silver allows to decrease the band gap energy of the semiconductor from 3.3 eV to 2.98 eV, thus increasing the photocatalytic activity of the material (Figures S2 and S3, Table S3). This phenomenon is also in accordance with the literature.<sup>28-32</sup> Indeed, Ag and TiO<sub>2</sub> form a Schottky barrier, that reduces the recombination rate of the e<sup>-</sup>/h<sup>+</sup> pairs, silver acting as an electron trap,<sup>28, 30, 32</sup> thanks to its lower Fermi level of 1.1 eV (Scheme 2).<sup>33</sup> According to several works, the silver species are composed of metal Ag<sup>0</sup>, which is known to stabilize the photocatalyst<sup>34</sup> and Ag<sup>+</sup> species, that come from partial oxidation of the photodeposited metal in air.<sup>29, 34, 35</sup> The heterojunction construction described in Scheme 2 avoids the recombination of the e<sup>-</sup>/h<sup>+</sup> pairs,<sup>30, 36</sup> probably thanks to the presence of Ag<sup>+</sup> species,<sup>34</sup> and therefore improves the activity. Moreover, no conversion was observed with TiO<sub>2</sub> alone, thus proving that doping the surface with silver is crucial to specifically activate N<sub>2</sub>O and produce the N<sub>2</sub>O<sup>-</sup> radical anion species [Equations (2) and (3)].<sup>26</sup> The formation of radical intermediates was also corroborated by performing the reaction in the presence of radical scavengers (Table S6 and Figure S10). This radical anion compound (N<sub>2</sub>O<sup>-</sup>) can reversibly adsorbed on Ag<sup>+</sup>, with formation of Ag-N<sub>2</sub>O complex [Equation (3)] as already reported over a Ag<sup>+</sup>/ZSM-5 catalyst.<sup>37</sup> Then, transfer of oxygen from the adsorbed N<sub>2</sub>O (N<sub>2</sub>O<sub>ads</sub>) on silver to the phosphine occurs on the hole site, to produce the corresponding oxide, with release of N<sub>2</sub> from nitrous oxide and regeneration of the silver active species [Equation (4)]. This proposed mechanism is supported by the favorable redox potential of PPh<sub>3</sub>/OPPh<sub>3</sub> (-2.9 V vs. Fc/Fc<sup>+</sup>).<sup>38</sup>

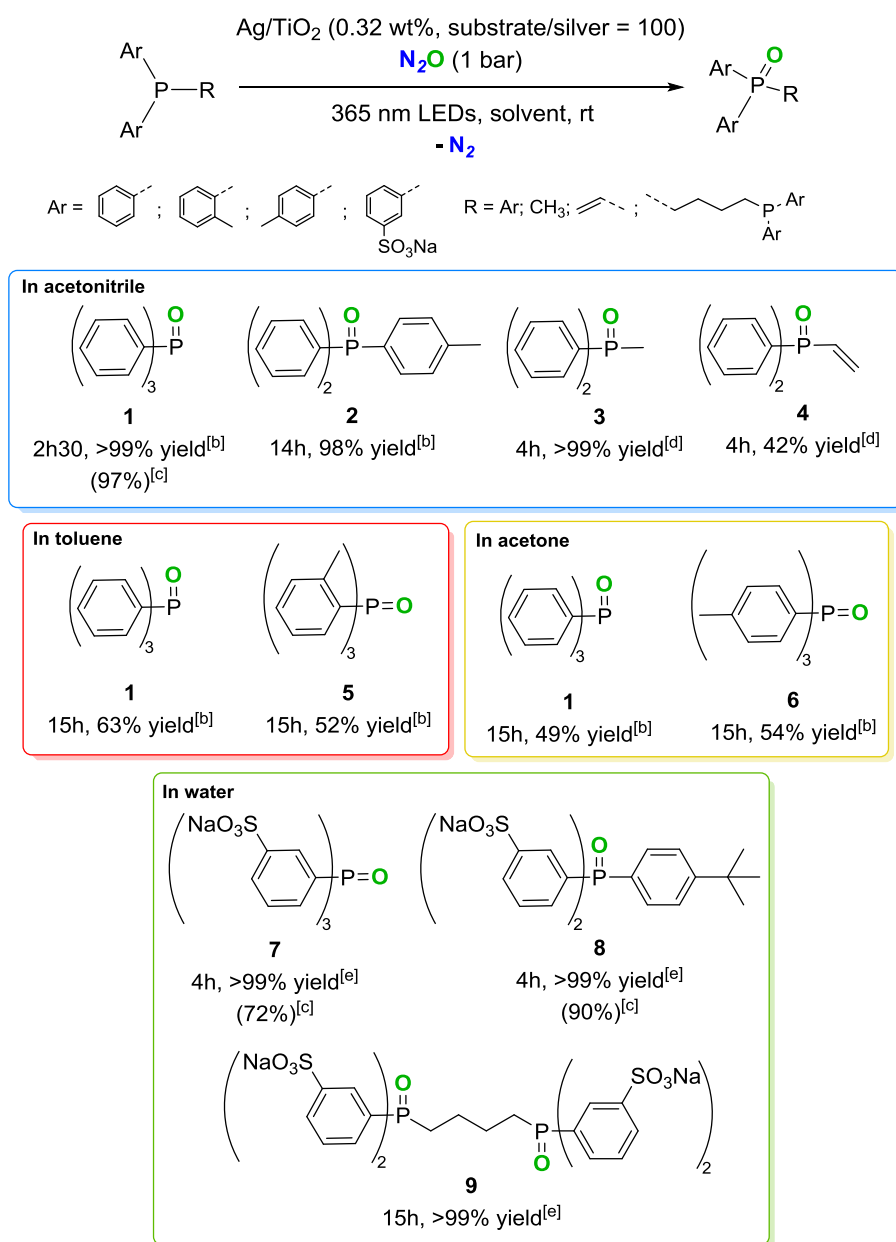


**Scheme 2.** Proposed mechanism for phosphine oxidation by N<sub>2</sub>O adsorbed on Ag/TiO<sub>2</sub>. CB and VB values are giving in eV vs. NHE.



Interestingly, same photocatalytic activities were achieved under similar conditions, using either the Ag/TiO<sub>2</sub> photocatalyst or TiO<sub>2</sub> alone, but under a dioxygen atmosphere (Table S5). These results prove the pivotal role of the silver deposited on the TiO<sub>2</sub> surface to specifically activate nitrous oxide, while being bystander towards oxidation reactions with O<sub>2</sub>. Remarkably, the oxidation reaction is extremely selective under N<sub>2</sub>O, with complete conversion of triphenylphosphine into the corresponding oxide **1** in 2.5 h (Table 1), and no photodegradation of triphenylphosphine oxide even after 15 h of irradiation (Table S5). Oppositely, a complete conversion was obtained under O<sub>2</sub> after 2 h, followed by the significant formation of carbon dioxide detected by GC-BID (Barrier Ionization Discharge) detector (0.25 equivalent, Table S5), that indicates the mineralization of the phosphine oxide. Indeed, photocatalytic systems based on TiO<sub>2</sub> under oxygen atmosphere are known for the degradation of organic compounds into CO<sub>2</sub> and water.<sup>27</sup> Herein, we evidence that N<sub>2</sub>O is more selective than O<sub>2</sub>, with only oxygen transfer to the phosphorus atom of the phosphine, without possible photodegradation of the product formed.

**Table 1.** Photocatalytic oxidation of different phosphines with N<sub>2</sub>O in various solvents.<sup>[a]</sup>

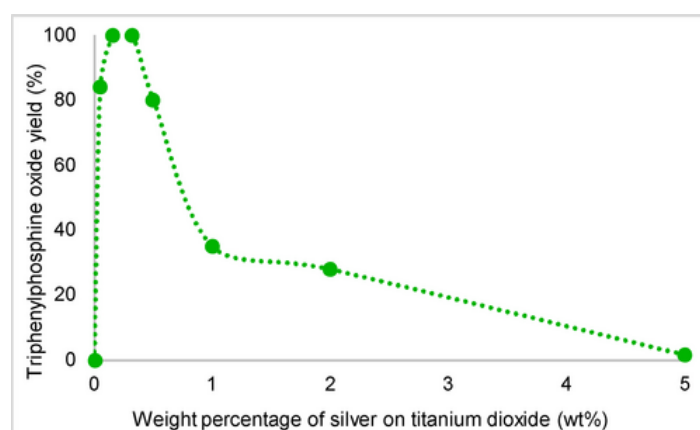


[a] Reactions conditions: catalyst Ag/TiO<sub>2</sub> (100 mg, 0.32 wt % Ag), substrate (0.24 mmol), substrate/silver molar ratio=100, 1 bar of pure N<sub>2</sub>O (0.29 mmol in gas phase, 7 mL), 3 mL of solvent, 365 nm irradiation (two LEDs, 150 mW/cm<sup>2</sup>), room temperature. [b] Determined by GC with 1,2-dichlorobenzene as external standard. [c] Isolated yield. [d] Relative proportion of the peak area obtained by GC. [e] By <sup>31</sup>P NMR.

Designing the optimum catalyst for this transformation is also a key step to achieve the higher photocatalytic activity, thus optimizing several parameters, such as the silver precursor salt or the type of TiO<sub>2</sub> (Figure S11). Titanium dioxide P25 (mixture of 70 % of anatase and 30 % of rutile) as support for silver nanoparticles (Ag-NPs) afforded higher activity compared to anatase or rutile alone, thanks to the combination of their advantages in terms of electronic properties and pore size

distribution.<sup>39</sup> Concerning the effects of the silver precursor, higher performances were achieved with silver nitrate ( $\text{AgNO}_3$ ) on P25, compared to silver sulfate or silver oxide (Figure S11). Moreover, the photodeposition on  $\text{TiO}_2$  performed with  $\text{AgNO}_3$  provides smaller particle sizes and a better dispersion of Ag-NPs on the support,<sup>35</sup> leading to a more active catalyst.

Finding the optimum Ag loading is also essential to avoid a poisoning effect for a suitable light irradiation excitation and to afford efficient photooxidation performances. Moreover, the ratio of  $\text{Ag}^0$  could increase with the silver loading by aggregation, at the expense of  $\text{Ag}^+$ , thus decreasing the catalytic activity.<sup>32</sup> Figure 3 shows that the oxygen transfer from  $\text{N}_2\text{O}$  to  $\text{PPh}_3$  was optimum for a silver loading between 0.16 and 0.32 wt % with a quantitative yield in the corresponding oxide after 2 h of LED irradiation. For higher metal loadings, the catalytic activity quickly decreased with no conversion observed with 5 wt % of Ag after 2 h. Therefore, following catalytic reactions were performed with a semiconductor doped with a 0.32 % wt. Ag, and a substrate/silver molar ratio of 100. The system was also found to be active at lower silver loading (Figure S12), with a complete conversion with 0.5 mol% of silver in 6 h.



**Figure 3.** Influence of Ag weight percentage on the activity. Reaction conditions: catalyst  $\text{Ag}/\text{TiO}_2$ , triphenylphosphine (0.24 mmol), substrate/silver molar ratio=100, 1 bar of pure  $\text{N}_2\text{O}$  (0.29 mmol in gas phase, 7 mL), 3 mL of  $\text{CH}_3\text{CN}$ , 365 nm irradiation (two LEDs,  $150 \text{ mW}/\text{cm}^2$ ), 2 h, room temperature.

Triphenylphosphine oxide yield determined by GC-FID with 1,2-dichlorobenzene as external standard.

Acetonitrile was chosen as a common solvent in photocatalytic reactions, being inert towards the system and able to solubilize  $\text{PPh}_3$ . Moreover, nitrous oxide presents a good solubility in this solvent, as experimentally determined ( $2.5 \times 10^{-2} \text{ mol}/\text{L}$ , Table S8). The reaction was also performed in other organic solvents (trifluorotoluene, benzene, cyclohexane, etc., Table S7) according to substrate's solubility (Table 1), and suitable solubility of  $\text{N}_2\text{O}$  (Table S8), but with different kinetics for oxygen transfer to the phosphine. In fact, triphenylphosphine was totally transformed in the corresponding oxide (**1**) within  $\text{CH}_3\text{CN}$  with an isolated yield of 97 % in 2.5 h, while the photocatalytic activity was much lower in toluene with a 63 % yield in 15 h. Oxygen transfer from  $\text{N}_2\text{O}$  to tris(*o*-tolyl)phosphine



(5) and tris(*p*-tolyl)phosphine (6) were performed in toluene and acetone respectively, in regards to their low solubility in acetonitrile. The substitution by a methyl group on the aromatic ring lowered the activity due to a more steric hindrance (2, 5). Interestingly, the reaction is chemoselective in the case of diphenylvinylphosphine (4), with oxygen transfer only on the phosphorus atom and the competitive vinylic group being untouched. Remarkably, the system was also very active in water, a green and benign solvent, with complete conversion of water-soluble phosphines, such as TPPTS (3-bis(3-sulfonatophenyl)phosphanylbenzenesulfonate trisodium salt), DPPBTS (tetrasulfonated 1,4-bis(diphenylphosphino)butane), or *t*BuTPPDS (bis(3-sodium sulfonatophenyl)(4-*tert*-butylphenyl)phosphine), a mixed aryl sulfonated phosphine, into the corresponding oxides (7–9). For these substrates, selectivity is preserved and no CO<sub>2</sub> formation was evidenced by GC-BID analysis, thus no mineralization of the oxidation products occurred. To our knowledge, no quantitative oxidation of sulfonated phosphines has been yet reported under light irradiation in water.

## Conclusion

In conclusion, various phosphines were used as molecular probes to harness the efficient oxygen transfer from nitrous oxide and validate its efficient photoactivation. This study constitutes a proof-of-concept of the use of this greenhouse effect gas as a selective oxidative agent in organic synthesis, as well as its efficient upgrading in mild conditions instead of thermal degradation. Silver on TiO<sub>2</sub>, easily prepared by a straightforward photodeposition process, specifically activates N<sub>2</sub>O at a very low metal loading (0.16 wt %). Photocatalytic oxygen transfer from N<sub>2</sub>O to different phosphines is performed at room temperature and atmospheric N<sub>2</sub>O pressure under an easy and clean process, either in organic solvents or in water, with N<sub>2</sub> as sole by-product. This study is ongoing to extend the reaction to others more challenging but also value-added substrates, for instance for the oxidation of hydrocarbons.

## Experimental Section

### Chemicals

All chemicals were purchased from Acros Organics (Illkirch, France) or Sigma-Aldrich-Fluka (Saint-Quentin-Fallavier, France). Nitrous oxide 99.99 % purity was purchased from Air Liquide (Paris, France). All these starting materials were used without further purification. Water was distilled twice before use by conventional method. Organic solvents were all HPLC grade.

### Synthesis of silver on titanium dioxide

In a round bottom flask, an adequate amount of titanium dioxide (250 mg–8 g) was added to 80 mL of an aqueous silver nitrate ( $2.10^{-5}$ – $1.10^{-4}$  mol) solution under stirring, the quantities of each compound depending on the silver amount (between 0.05 and 5 wt % of silver). The pH was adjusted to approximately 6.3 by addition of a few drops of an acetic acid solution ( $0.1 \text{ mol.L}^{-1}$ ) or a potassium hydroxide solution ( $0.1 \text{ mol.L}^{-1}$ ). After 15 min under stirring, 4 mL of methanol were added and the suspension was irradiated by a UVA lamp (Philips) for 4 hours, under continuous argon bubbling flow and vigorous stirring. The solid product was recovered by filtration of the suspension, washed several times with re-distilled water under air atmosphere, and dried under vacuum at  $100 \text{ }^{\circ}\text{C}$  for 1 h30. The obtained purplish photocatalyst was grinded manually, and stored in argon and away from the light.

### **Characterization**

Characterization methods for both catalysts (ICP, XRD, BET, UV, TEM) and organic compounds (GC, NMR) are detailed in the Supporting Information.

### **Photocatalytic experiments**

Photocatalytic experiments were performed at room temperature under nitrous oxide atmosphere (1 bar). A 10 mL Schlenk tube, closed by a septum and containing the right amount of photocatalyst, is filled with nitrous oxide (three vacuum-nitrous oxide cycles) while stirring with a cross-shape magnetic stirrer. 3 mL of a solution of the substrate (triphenylphosphine or derivatives) in the adequate solvent, that has been previously bubbled and stored under nitrous oxide atmosphere, was added with a syringe. After stirring for 30 to 60 min in the dark to reach adsorption equilibrium conditions, the reactor was irradiated by two LED lamps at 365 nm with an average intensity around the reactor of  $150 \text{ mW/cm}^2$ . Due to the light irradiation, the temperature of the media reached  $38 \text{ }^{\circ}\text{C}$  after 15 min and remained stable afterwards. Before and after the reaction, gas phase samples were collected with a  $100 \text{ }\mu\text{L}$  (*i. e.* 1 % of the total volume of the vessel) Hamilton Gastight SampleLock syringe, equipped with a syringe guide, and analysed by GC for quantification (details in the supporting information). The syringe was left open and purged three times with air between each sampling. After the reaction, the reactor was opened to air and the solution was filtered through a  $0.20 \text{ }\mu\text{m}$  syringe filter to remove the catalyst. The solution was then analysed by GC for quantification (details in the supporting information), and/or by  $^{31}\text{P}$  NMR (spectra acquired on 400 MHz Bruker instruments at the Ecole Nationale Supérieure de Chimie de Rennes).

**Acknowledgements:** This work was supported by the Ministère de l'Enseignement Supérieur et de la Recherche (grant to O.D.). The authors are grateful to Bertrand Lefeuvre from UMR-CNRS 6226, Université de Rennes 1 for ICP analysis and to Sandra Casale from the Service de Microscopie

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